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INDUSTRIAL CHEMISTRY

BEING A SERIES OF VOLUMES GIVING A
COMPREHENSIVE SURVEY OF

THE CHEMICAL INDUSTRIES

EDITED BY SAMUEL RIDEAL, D.Sc. LOND., F.I.C.
FELLOW OF UNIVERSITY COLLEGE, LONDON

ASSISTED BY

JAMES A. AUDLEY, B.Sc.
W. BACON, B.Sc., F.I.C.
M. BARROWCLIFF, F.I.C.
H. GARNER BENNETT, M.Sc.
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W. H. SIMMONS, B.Sc.
R. W. SINDALL, F.C.S.
D. A. SUTHERLAND, F.C.S.
C. M. WHITTAKER, B.Sc.
&c., &c.

MODERN DYEING METHODS

THE APPLICATION OF THE COAL TAR DYESTUFFS

THE PRINCIPLES INVOLVED AND THE METHODS EMPLOYED

BY

C. M. WHITTAKER, B.Sc.

FOR SEVENTEEN YEARS HEAD OF THE EXPERIMENTAL DYEHOUSE OF MESSRS. READ HOLLIDAY AND SONS, LTD., HUDDERSFIELD, NOW BRITISH DYES, LTD.

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GENERAL PREFACE

THE rapid development of Applied Chemistry in recent years has brought about a revolution in all branches of technology. This growth has been accelerated during the war, and the British Empire has now an opportunity of increasing its industrial output by the application of this knowledge to the raw materials available in the different parts of the world. The subject in this series of handbooks will be treated from the chemical rather than the engineering standpoint. The industrial aspect will also be more prominent than that of the laboratory. Each volume will be complete in itself, and will give a general survey of the industry, showing how chemical principles have been applied and have affected manufacture. The influence of new inventions on the development of the industry will be shown, as also the effect of industrial requirements in stimulating invention. Historical notes will be a feature in dealing with the different branches of the subject, but they will be kept within moderate limits. Present tendencies and possible future developments will have attention, and some space will be devoted to a comparison of industrial methods and progress in the chief producing countries. There will be a general bibliography, and also a select bibliography to follow each section. Statistical information will only be introduced in so far as it serves to illustrate the line of argument.

Each book will be divided into sections instead of chapters, and the sections will deal with separate branches of the subject in the manner of a special article or monograph. An attempt will, in fact, be made to get away from the orthodox textbook manner, not only to make the treatment original, but also to appeal to the very large class of readers already possessing good textbooks, of which there are quite sufficient. The books should also be found useful by men of affairs having no special technical knowledge, but who may require from time to time to refer to technical matters in a book of moderate compass, with references to the large standard works for fuller details on special points if required.

To the advanced student the books should be especially valuable. His mind is often crammed with the hard facts and details of his subject which crowd out the power of realizing the industry as a whole. These books are intended to remedy such a state of affairs. While recapitulating the essential basic facts, they will aim at presenting the reality of the living industry. It has long been a drawback of our technical education that the college graduate, on commencing his industrial career, is positively handicapped by his academic knowledge because of his lack of information on current industrial conditions. A book giving a comprehensive survey of the industry can be of very material assistance to the student as an adjunct to his ordinary textbooks, and this is one of the chief objects of the present series. Those actually engaged in the industry who have specialized in rather narrow limits will probably find these books more readable than the larger textbooks when they wish to refresh their memories in regard to branches of the subject with which they are not immediately concerned.

The volume will also serve as a guide to the standard literature of the subject, and prove of value to the consultant, so that, having obtained a comprehensive view of the whole industry, he can go at once to the proper authorities for more elaborate information on special points, and thus save a couple of days spent in hunting through the libraries of scientific societies.

As far as this country is concerned, it is believed that the general scheme of this series of handbooks is unique, and it is confidently hoped that it will supply mental munitions for the coming industrial war. I have been fortunate in securing writers for the different volumes who are specially connected with the several departments of Industrial Chemistry, and trust that the whole series will contribute to the further development of applied chemistry throughout the Empire.

SAMUEL RIDEAL.

AUTHOR'S PREFACE

THE application of the coal tar dyestuffs to the textile fibres is so varied and the combinations of these fibres in textile fabrics are becoming so increasingly varied that one is immediately confronted with the difficulty of condensing into a reasonable space any book dealing with this subject. The writer has, therefore, decided to confine himself to the essential principles involved, and the methods employed in the application of the coal tar dyestuffs.

Typical examples only of the various classes of dyestuffs are given to illustrate the principles of their application; complete lists of dyestuffs are purposely omitted in order to avoid making the book appear to be a catalogue of the various colour-makers' dyestuffs. Such lists would overload the book and create the danger of hiding the essential facts under a mass of non-essential details. Moreover, such lists soon become out of date. For the same reason no attempt is made to deal with the various types of machines used in the dyeing industry. The choice of a suitable machine is determined by two factors, viz, the class of material to be dyed and the class of colour to be used. The writer's experience of seventeen years has taught him that no single machine will do all classes of work, but that each machine has its defects for certain classes of work. Local conditions must therefore largely determine the choice of a machine.

This book has been written with a view to giving the reader a firm grasp of the chemical principles involved, and the methods used in the application of the coal tar dyestuffs, so that when he commences to carry out dyeing under actual commercial conditions he will know the why and the wherefore of the methods employed. Many of the pitfalls awaiting the novice are indicated, but it must always be remembered that no book, however detailed, can make a successful dyer.

C. M. WHITTAKER.

HUDDERSFIELD,
June, 1918.

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INDUSTRIAL CHEMISTRY

Being a Series of Volumes giving a Comprehensive Survey of

THE CHEMICAL INDUSTRIES.

Edited by SAMUEL RIDEAL, D.Sc. (Lond.), F.I.C., Fellow of University College, London.

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COAL TAR DYESTUFFS

SECTION 1.—GENERAL SURVEY OF DYEING

HISTORICAL researches show that dyeing was practised in the earliest times, centuries before the Christian era. It is highly probable that indigo was the earliest dyestuff known to man, and its dyeing is known to have originated in India in the dim past, when crude fermentation vats were and still are used, and its use has spread from there to all parts of the globe. Again, the analysis of mummy cloths has revealed the familiarity of the Egyptians with aluminium mordant, weld, etc., whilst it is commonly known that the patrician purple was obtained from a shellfish.

In the middle ages dyers were combined in guilds, which were maintained by definite and strict rules as to the methods to be employed. Many interesting publications on these guilds are open to those who wish to delve in this branch of the subject, but this is a book on modern dyeing principles, so the above are only referred to *en passant.*

Before the introduction of the coal-tar dyestuffs dyers had but a limited range of natural vegetable products and chemicals at their disposal, with which they were able to dye a variety of shades, which every fair-minded person must admit was a credit to them, however much people may scoff at them as rule-of-thumb men. Indeed one might with every fairness claim that the practical and exclusive knowledge possessed by the old-time dyer, acquired by long practice and patient observant study of the natural dyestuffs, was a very potent factor in the early development of our textile industries, thereby setting that standard in the world's markets for British goods which was universally recognized as the best which could be produced at the time. This factor in the evolution of our textile industry has usually been overlooked by every writer on the subject. It has certainly never been appreciated at its true worth.

The chief products which were used were as follows:—Logwood, in combination with chromium or iron, gave blacks on silk and wool, the shades of which all the coal-tar colours yet discovered have not been able to surpass for beauty of shade, but the coal-tar blacks have far surpassed logwood blacks in fastness to light and acids. On cotton logwood, in combination with tannin (myrabolans) and copperas, was used for blacks.

Indigo was the basis of all fast blues, and in combination with logwood and fustic gave the woaded blacks and greens, which were dyed on the old-fashioned broadcloths. For cheaper blues logwood was used, whilst Prussian blue was also used, which was very fast to light and a beautiful shade, but had the fatal defect of not being fast to alkali.

Madder was used on alum mordant for the famous turkey red on cotton, and on chrome mordanted wool for madder reds. Cochineal on tin mordant gave the bright scarlets which were used for hunting coats, and until quite recently for military uniforms. Camwood and barwood were also used for reds.

Cutch was and still is used for fast browns on cotton. Weld, flavin, fustic and Persian berries were used as yellows, whilst tannin, galls and myrabolans, in conjunction with iron, tin, antimony salts were and still are used as mordants on cotton for the various woods.

The chemicals used were various salts of chromium, iron, aluminium, tin, lead, antimony and copper: by skilful mixing of these mordants, coupled with the above products, a most varied range of shades was obtained.

In addition to the shades obtained with the above vegetable products a limited number of mineral colours were also used, such as Prussian blue, iron buff, chrome yellow and orange.

With the exception of logwood, fustic and cutch, all the above products have been supplanted by coal-tar dyestuffs. Madder has been completely supplanted by its synthetic form alizarine. Natural indigo was before the war almost completely supplanted by synthetic indigo.

Logwood and fustic have held their own owing to their cheapness and the beauty of tone of the former, but they were continuously losing ground prior to the war owing to their inability to be applied by the topchroming or metachrome processes, which are so much quicker than the chrome mordant process. Cutch and iron buff still hold their own.

Dyeing has been well defined as applied chemistry, and this is becoming more true every day, as the reader will realize as I develop this theme in the next few pages. Modern dyeing demands of the present-day dyer an increasing knowledge both of advanced organic and inorganic chemistry. Not only does the dyer require to have all the expert knowledge of materials and knowledge of the preparatory and finishing processes through which the material passes, but he has also to possess a sufficient knowledge of chemistry to understand the chemical processes involved in the application of modern coal-tar dyestuffs. I have often heard the statement made that the coal-tar colour firms, with their constant flow of new colours, their expert service, and their sumptuous volumes of instructions, have depreciated the position of the foreman dyer. I contend that this is a very superficial view to take, because all the pattern cards and most detailed instructions issued can never give a person the requisite practical knowledge without which no one can ever be a master or foreman dyer.

To prove this an average person need only take a recipe out of a pattern card, go into a dyehouse and attempt to get the same result. Such an attempt would prove disastrous and would serve to emphasize the necessity of leaving dyeing to the foreman dyer.

The discovery of mauve by Perkin in 1856 was epoch-making in its effects on dyeing. Perkin was, of course, no dyer, but he got in touch with practical dyers, who showed him how mauve could be applied to the various fibres. As regards application to cotton, mauve did not involve any new dyeing methods, because it fell in with the regular procedure of mordanting cotton with tannin and fixing with various metallic salts. Mauve was quickly followed by other basic dyestuffs, like magenta, in 1859, which enabled the dyer to obtain in a single operation shades which had been hitherto unobtainable. They, however, left a great deal to be desired in the way of fastness, which was the cause of a slow-dying prejudice against "anilines."

The next advance was the introduction of the spirit rosaniline blues, which had to be dissolved in methylated spirits previous to adding to the dyebath. The discovery soon followed in 1862 of making them soluble by treatment with concentrated sulphuric acid, which enabled wool and silk to be dyed brilliant shades from a simple acid bath. This was a great advance in simplifying dyeing, and the colours known commercially as Nicholson, water or soluble blue had a great vogue, and indeed are still of the greatest service in the silk, shoddy, jute, paper and ink-making industries. It is at first sight a curious fact that, after the success of soluble blues, it was not till 1877—fifteen years later—that acid magenta was patented, but this was no doubt due to the fact that fuming sulphuric acid is necessary for the successful sulphonation of magenta, and fuming sulphuric acid was at that time more or less of a chemical curiosity.

The next step was the discovery of the diazo reaction in 1876 by Peter Griess at Burton. It may safely be asserted that this discovery has had more influence than any other chemical reaction used in coal-tar chemistry, because the possible combinations of azo dyestuffs are without limit, and hundreds are definite commercial successes in the dyeing trade. The range of acid, direct cotton and mordant dyestuffs made by this reaction include practically every shade required, and their introduction and gradual development revolutionized dyeing methods in several branches, such as knitting yarn, carpet yarn, dress goods, cotton goods, etc. Meantime the synthesis of alizarine in 1868–69, whilst not altering methods of dyeing except as to gradually displace all mordants for wool except chromium, had the effect of placing at the disposal of the dyer a range of shades which were superior in fastness to light to the old wood colours. The methods of application did not involve any great variation from the methods already employed, though the bisulphite compounds of the alizarine dyestuffs involved special precautions.

The patent taken out in 1871 by Schutzenberger and Lalande for the dyeing of indigo in the hydrosulphite vat has gradually had the effect of introducing the definite chemical method of dyeing indigo under chemical control, as compared with the old fermentation vats, which demanded great skill and experience to keep them under control. The next class of dyestuffs to be introduced on the market were the azoic dyestuffs (azo dyestuffs actually produced on the fibre), which were patented by Messrs. Thomas and Robert Holliday in 1880. This class of dyestuffs involved quite a new principle in dyeing, in that the process consisted of making the actual colour itself on the fibre, and thus converted willynilly those dyers who used the process into actual colour makers, and so demanded from them a knowledge of colour chemistry, which had not hitherto been expected from them.

The next step forward—the introduction of direct cotton dyestuffs in 1884—led to a great simplification of the cotton dyer's work and to the development of single bath union dyeing, and as a natural corollary modern garment dyeing. How useful these dyestuffs have been is revealed by the Dyestuff Census of U.S.A., because they had the largest annual consumption of any class of dyestuff. The discovery of primuline in 1887 again widened the chemical outlook of the dyer by introducing the diazotizing and developing process to commercial dyeing. The dyer had to understand the reason why diazotizing must be carried out cold, and why diazotized material must be protected from light and heat: he had also to learn that certain developing baths had to be alkaline, whilst others had to be acid. The same remarks apply to the coupling with diazotized paranitraniline process.

A great advance was the discovery of the sulphur dyestuffs in 1893 by M. Vidal, which greatly simplified the production of fast shades on cotton, but this again placed greater demands on the chemistry of the dyer in that he had to dye with leuco compounds, which he must see were in a perfectly reduced state, yet not too soluble, so that it would not dye on the fibre, whilst it involved careful handling of the material in order to get level results.

The introduction of the Metachrome process for the application of certain mordant dyestuffs in 1900 again made it requisite for the foreman dyer to understand the chemical reactions taking place in the dyebath in order to get successful results, though when thoroughly understood it led to simplification of his work.

Finally, the introduction of the vat dyestuffs in 1901 made perhaps the biggest demand of any class of dyestuffs on the skill and chemistry of the foreman dyer.

The above short résumé clearly illustrates that though dyeing processes have been simplified it has also made an increasing demand upon the chemical knowledge of the dyer, and the new classes of dyestuffs instead of depreciating the dyer's status are increasing it. True the old secrecy of recipes, etc., has passed away, but no recipe, however elaborately bound in gilt and leather, ever made a dyer.

Passing on to the question of fast and loose dyestuffs it is necessary to thoroughly grasp the fact that there is no such thing as absolute fastness as applied to dyes, yet I have been repeatedly asked in the course of business if a certain shade is absolutely fast. It is essential to realize that fastness is purely relative, not absolute. If experience has proved that a dyestuff during the lifetime of a fabric withstands all influences to which that fabric is subjected, then the dyer designates that dyestuff as fast for that particular class of goods. The range of fastness for which dyers have to cater is extraordinarily wide and varied, and it is this fact which makes all terms of fastness *re* dyestuffs purely relative. This may be illustrated by choosing two extreme instances. A lady's ball dress is never exposed to daylight, and the only process through which it may be passed is drycleaning, therefore the most fugitive dyestuffs may safely be termed fast for ball fabrics: on the contrary, a naval uniform is exposed to the severest conditions extant, viz. sunlight and exposure to sea air, therefore the fastest obtainable colours must be used for this purpose—in fact, indigo is used, but even this gradually suffers under these influences.

One is justified in saying that the nearest approach to absolute fastness is made by some of the modern vat dyestuffs, in that they will last longer than the cotton on which they are usually dyed, *i.e.* the fabric perishes before the colour has faded: yet these dyestuffs will not withstand boiling under pressure with caustic soda without bleeding on to adjacent white.

These examples suffice to show that in considering the fastness of dyestuffs it is always necessary to lay down two conditions, viz. :—

1. For what purpose is the fabric on which the dyestuff has to be dyed going to be used?

2. To what influences is the dyestuff required to be fast?

It is no use putting good and therefore expensive colours on to cotton cloth which is going to be used for linings: on the contrary, it is no use putting colours not fast to washing into shirtings.

It follows logically from this that different sections of the dyeing industry have entirely different standards of fastness, which apply to their respective sections only. This explains why different dyers hold such widely different views of the fastness of one and the same dyestuff. The dyeing industry is necessarily essentially commercial, so that price is the ruling factor, from which it follows that for the dyeing of shoddy cloth, which is sold at 1*s.* 6*d.* a yard, a much lower grade of dyestuffs must be used than those used in dyeing the best worsted overcoating, which will sell at 15s. a yard. From the above it will be seen that the terms fast and loose are purely relative in the dyeing industry. It ought also to be realized that the bulk sales in the coal-tar dyestuff industry are of the cheap and loose colours, and not of the expensive and fast colours. A great deal has been written about the necessity of the British industry making the fast colours made in Germany, but few people realized that the sales of these colours were insignificant as compared with the sales of the commoner or less fast dyestuffs. The following concrete instances from the United States Dyestuff Census will illustrate the above statement: 36,674 lbs. benzo fast scarlet (which is fast to light and acids) were imported as compared with 341,724 lbs. benzopurpurine 4B (which is fast neither to light nor acids), 10,917 lbs. alizarine rubinol R (very fast to light), were imported, against 160,252 lbs. azo rubine (nothing like as fast as rubinol), 953,411 lbs. developing and fast to light blacks compared with 4,104,175 lbs. common cotton blacks, which are not fast to light.

Moreover, fashion and modern custom have an important influence on the class of dyestuffs consumed. Some fashionable garments are so ephemeral that they are discarded before the dyestuff has been put to a severe test. Again, people now buy cheaper clothes often rather than expensive clothes at long intervals, so that fastness is neither looked for nor desired. Both these factors increase the consumption of the less fast and cheaper colours.

The trend of modern dyeing may be separated into five phases:—

1. The increasing adoption of mechanical and labour-saving appliances.
2. The constant demand for ease of application.
3. The increasing knowledge of chemistry required to thoroughly understand the application of the modern coal-tar dyestuffs.
4. The increasing number and variety of fabrics made

from combinations of silk, wool, cotton and artificial silk.

5. The increasing call on the dyer and colour manufacturer for dyes capable of withstanding processes during manufacture: thus allowing for cloths of new or improved quality to be manufactured.

The dyeing industry in its increasing adoption of machines is only following the economic conditions ruling in all industries at the present day, viz. that increased cost can only be met by increased production. This explains why machines capable of dyeing 1200–1400 lbs. of wool are now being adopted, whereas 250 lbs. only was formerly dyed at a time.

Machines capable of dyeing 2000 lbs. of loose cotton at a time are also quite common features in loose cotton dyehouses. The desire to economize labour is also responsible for the increasing number of machines for the dyeing of yarn in the form of cops, cheeses and beams, which are being steadily adopted in order to avoid the winding of the yarn into hanks and then re-winding into the cop, etc.

From the first phase it is a logical step to phase two. Since modern economic conditions are always enforcing economy in labour, time and steam, it is a natural sequence that the dyeing industry is always on the lookout for colours which have the simplest and quickest method of application. It is also obvious that the less the material is handled the less does it depreciate in condition. Again, dyeing machines demand soluble colours, because otherwise the material simply acts as a filter when the dye-liquor is circulated, and all the dyestuff collects on the outside of the material—for this reason alizarine dyestuffs are unsuitable for machine dyeing owing to their insolubility. Moreover, dyestuffs which dye on slowly are also desirable, or else the outside of the material will be dyed much heavier than the centre.

The third phase has already been discussed. The fourth phase is explained by two facts. The steady improvement in the quality of artificial silk, coupled with its reduction in price and the increasing experience in weaving it in conjunction with other fibres, has led to an ever widening use of artificial silk in union goods.

The ever-present demand for cheapness must always be recognized, however much one may regret it. Big production in modern industry takes the form of a cheap, not a dear, article. A constant endeavour is being made by cloth designers to make as good an imitation as possible of a costly fabric in a cheaper material. This explains why one now meets so many fabrics which contain wool and cotton to imitate at a low price the more expensive all-wool article. To give an example, a cotton warp is woven with a woollen weft in a serge pattern to imitate an all-woollen serge. These fabrics have naturally to be coloured, and reflect themselves in the increasing demand for union dyestuffs, which has been one of the most striking modern features in the coal-tar dyestuff industry. Moreover, such union fabrics demand great skill on the part of the dyer to produce the desired result. It will easily be understood that it is much more difficult to produce a good result on a wool and cotton fabric than producing a similar result on an all-wool article.

The final phase may be illustrated by the demand for colours which will withstand the severe processes of crabbing, steaming and cross-dyeing, *i.e.* boiling with acids, or the demand for colours which will withstand kier boiling and chemick. The production of such shades throws an added strain on the dyer, because a faulty dyeing may produce endless trouble in the subsequent stages of manufacture, which may result in very heavy claims for damages.

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" Die Apparatfärberei." Ullman.
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" Khaki auf Baumwolle." Theis.
" Indigo und Seine Concurrenten." Felsen.
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In addition to the above a very large amount of literature is distributed gratis by the dyestuff manufacturers. Whilst this is naturally confined to the individual manufacturer's dyestuffs, the methods described will be found to be reliable and completely up-to-date.

CURRENT PUBLICATIONS

The Dyer and Calico Printer.
The Journal of the Society of Dyers and Colourists.
The Journal of the Society of Chemical Industry.
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The Textile Manufacturer.
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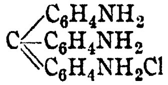
Deutsche Färber Zeitung.
Deutsche Färber Kalendar.
Leipziger Färber Zeitung.
Zeitschrift für Textil Chemie.

SECTION II.—THE BASIC DYESTUFFS

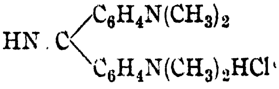
FROM the standpoint of this book the Basic Dyestuffs are one class; from the point of view of the chemist they consist of the following classes:—

Triphenylmethane Magenta :



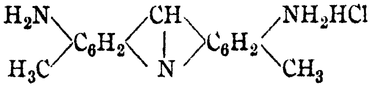
$$C\begin{cases}C_6H_4NH_2\\C_6H_4NH_2\\C_6H_4NH_2Cl\end{cases}$$

Diphenylmethane Auramine :



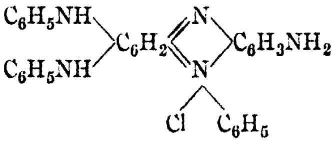
$$HN\,.\,C\begin{cases}C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2HCl\end{cases}$$

Acridine—Acridine Yellow :



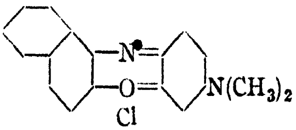
$$\begin{matrix}H_2N\\H_3C\end{matrix}>C_6H_2<\begin{matrix}CH\\|\\N\end{matrix}>C_6H_2<\begin{matrix}NH_2HCl\\CH_3\end{matrix}$$

Indamine—Indamine Blue :

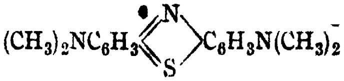


$$\begin{matrix}C_6H_5NH\\C_6H_5NH\end{matrix}>C_6H_2<\begin{matrix}N\\ \\ \underset{Cl\quad C_6H_5}{N}\end{matrix}>C_6H_3NH_2$$

Oxazine Meldola's Blue :

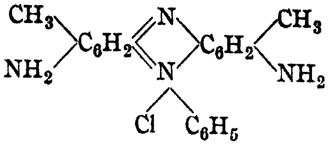


Thiazine Methylene Blue :

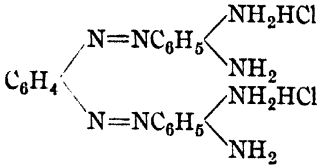


$$(CH_3)_2NC_6H_3<\begin{matrix}N\\S\end{matrix}>C_6H_3N(CH_3)_2$$

Azine Suffranine :



Azo Bismarck Brown :



The Basic Dyestuffs are so called because of their basic character, which is derived from the amido groups, which are present in the dyestuffs as free amido groups or amido groups alkylated in varying degrees, usually $N(CH_3)_2$ or $N(C_2H_5)_2$. A glance at the formulæ of the above typical examples of the various chemical classes of Basic Dyestuffs will quickly illustrate this. They are usually put on the market as hydrochlorides, though some of them appear as the zinc double salt, whilst other acids are occasionally used, such as oxalic acid. They are also supplied as the free bases for the colouring of oils, fats, waxes, etc.

The Basic Dyestuffs were the earliest coal tar dyestuffs to be put on the market: mauve, the first coal tar dyestuff discovered in 1856, was a basic dyestuff. They met with a ready demand owing to their brilliancy of shade, coupled with great strength of colouring power. They unfortunately proved to be very fugitive and loose compared with the wood dyes, which were the standard colours of the dyeing industry at that period. This fact was, in the author's opinion, the reason why the stigma of being fugitive was still attached to the coal tar dyes long after extremely fast coal tar dyestuffs had been adopted in the dyeing trade. Not only are the Basic Dyestuffs fugitive to light—methylene blue being one of the fastest to light—but many of them are sensitive to acids, alkalies, stoving, and washing. Again, no method has yet been devised of dyeing them so that the resulting shades do not rub.

In addition to this the Basic Dyestuffs are in many instances extremely difficult to dye satisfactorily, owing to the fact that they are liable to yield bronzy results in heavy shades, whilst in pale shades the colours are liable to go on unevenly owing to their strong affinity for the fibre. From the above it will be readily understood that dyers are only waiting for adequate substitutes of equal brilliancy of shade in other classes of dyestuffs in order to stop using what to them are always troublesome colours. The necessary substitutes have, however, not yet been found, though some of the Direct Cotton Dyestuffs have come very close in brilliancy to the Basic Dyestuffs, whilst being superior in fastness to rubbing—I refer to the chlorazol brilliant blues, which give shades almost equal in brilliancy to methylene blue, whilst the benzo brilliant violets give shades closely approximating to the brilliancy of methyl violet and magenta. However, the defects of the Basic Dyestuffs are so well known to the trade that they are accepted as inevitable, and their use for certain shades has become standardized in many classes of goods. The Basic Dyestuffs have a pronounced affinity for silk, wool, jute, leather and paper, so that they find application on all these materials as well as cotton, linen and artificial silk. The last three fibres—with the exception of artificial silk, made from nitro-cellulose—have no direct affinity for these dyestuffs, so that they have to be given an artificial affinity by mordanting them in the manner detailed later in this section.

The Basic Dyestuffs in their application to wool and silk form the best evidence of what is termed the chemical theory of dyeing. The theory of dyeing is still in a very nebulous state, despite the voluminous nature of the literature on the subject. This is not surprising when one visualizes the intricacies of dyeing and the various classes of dyestuffs and methods of application employed.

There are three main theories of dyeing formulated—

1. The chemical theory.

2. The mechanical theory.
3. The colloid theory.

The first is generally accepted to apply more or less to the animal fibres, whilst the second is usually admitted to apply to the dyeing of cotton with Direct Cotton Dyestuffs. The colloid theory is not yet supported by sufficient evidence. Knecht showed by experiments that when wool or silk is dyed with magenta, the whole of the hydrochloric acid combined with the magenta is left in the dyebath at the end of the dyeing operation, thus showing that the acid group of the wool or silk has combined with the colour base of the magenta to form the dyed wool fibre. Georgievics has opposed, but not successfully, the work of Knecht, and states that there is a preliminary dissociation of the magenta into hydrochloric acid and a coloured ammonium base of rosaniline. If Georgievics' theory were correct, wool dyed with magenta would soon become decolorized if kept out of contact with air to prevent the formation in the fibre of carbonate of rosaniline (*vide* " A Manual of Dyeing," p. 9). In the case of jute the direct affinity of the Basic Dyestuffs is due to the amount of natural tannin contained in the jute fibre.

Cotton, linen, artificial silk (with the exception of the variety made from nitro-cellulose) and hemp have no affinity for the Basic Dyestuffs ; there are slight exceptions, *e.g.* Victoria blue B will dye unmordanted cotton a full shade from an acetic acid bath. These fibres have, therefore, to be previously mordanted with an acid mordant to combine with the basic group of the dyestuff.

APPLICATION.

Dissolving.—The Basic Dyestuffs are not distinguished for easy solubility, so that the greatest care must be exercised when dissolving them. The best way to dissolve them is to stir them into a perfectly smooth paste with cold water or acetic acid. This precaution prevents any dry colour floating on the top of the boiling water when added : any colour which so floats is liable to form itself into small balls of semi-tarry colour, which are extremely difficult to dissolve. Pour boiling water over the colour paste whilst stirring, and continue stirring until the colour has dissolved. The colour solution should not be actually boiled or else the colour is liable to become tarry, and it is very difficult to dissolve once it gets into this state. Condensed water should be used for dissolving Basic Dyestuffs when available.

Having dissolved the colour, the colour solution should never be added directly to the actual dyebath, but should be passed through a calico filter or fine mesh sieve in order to atch any undissolved particles of colour. If any such are llowed to pass into the dyebath they quickly attach themelves to the material and cause specks, which can only be emoved with the greatest difficulty.

Silk.—The Basic Dyestuffs are distinguished for their reat affinity for silk due to its pronounced acidity, on which bre they dye most brilliant shades, consequently they are argely used for fabrics for which no great fastness to light s required, such as ribbons, blouse silks, ball fabrics, etc.

They are best applied in a perfectly neutral bath or in boiled-off liquor bath just broken with acid. Acid in the yebath keeps the colour off the silk and prevents exhaustion. hould the water be hard this should be corrected with cetic acid, and any scum which may float on top of the yebath should be carefully removed before the silk is ntered. The silk is entered cold, worked cold 15–20 minutes, hen the temperature of the dyebath is gradually raised to 195° F. (90° C.), when the silk is lifted out and washed off. If trouble is experienced in obtaining level results then the following precautions should be taken : all the colour solution should not be added to the dyebath at the beginning, but the following mode of procedure should be adopted. The dyebath is charged with one-third of the colour solution and the silk worked in the cold bath till most of the colour has been absorbed; then add half of the remaining colour solution and the silk again worked till most of the colour is absorbed; finally the balance of the colour solution is added and the temperature of the dyebath gradually raised to 195° F. (90° C.). If the silk is scrooped (*i.e.* passed through a cold weak acid bath and wrung out without rinsing) after dyeing, it must be remembered that the shade of many Basic Dyestuffs is changed even by the weak acid used in this process, so that allowance must be made for this.

A very common test to which dyed silks are frequently submitted is the water test, which consists in steeping in cold water overnight. The colour must not stain the water or run on to adjacent material. The Basic Dyestuffs are by no means fast to this test, but their fastness may be considerably improved by the following after-treatment. Work the silk for 15 minutes at 140° F. (60° C.) in a bath charged with 5–10 lbs. tannic acid, then immerse and allow to steep overnight. Next morning wring out evenly and fix by working for half an hour in a fresh cold bath charged with 2½–5 per cent. tartar emetic, wash thoroughly and dry. This treatment has a dulling effect on the shade, so that allowance should be made for this when dyeing to pattern : a pure tannic acid should be used for this purpose in order to reduce the dulling effect to a minimum.

Tin-weighted Silk.—The Basic Dyestuffs have a good affinity for tin-weighted silk, so that no special precautions are necessary in dyeing this class of silk except to give the silk a wash in warm water to remove any unfixed metallic salt that may still remain on the fibre. It must also be remembered that tin-weighted silk which has been in stock for any length of time is very liable to give uneven results, owing to decomposition of the metallic weighting.

Wool.—The Basic Dyestuffs have lost and are continuing to lose a great deal of their importance in wool-dyeing, owing to the very large range of other classes of colours, notably acid dyestuffs, like acid magenta, acid violets, acid greens, etc., which enable the wool-dyer to get the same brilliant shades with colours which are more easily applicable. All Basic Dyestuffs cannot, however, be substituted by members of other classes of colours. I refer to Victoria blue, which is still largely used in wool, despite its marked fugitiveness to light. Its use is continued, because it yields shades from sky to royal blue of good fastness to milling and washing, which cannot be equalled in brilliancy by any other dyestuff.

Basic Dyestuffs are applied to wool in a perfectly neutral bath without any addition whatsoever. If pure water is available, soap may be used, when brighter shades will be obtained. Hard water should be corrected before use with acetic acid, otherwise the colour is liable to be precipitated in a tarry mass and so produce spots on the material, which it is practically impossible to subsequently remove. The wool is entered cold and worked cold 15–20 minutes, then the temperature of the bath is gradually raised to 195° F. (90° C.), when the colour will be found to be practically exhausted. If difficulty is experienced in getting level shades, take the precautions detailed under silk.

Victoria blue B will dye wool in a similar manner to acid dyestuffs, and it is usually dyed this way and not in the way detailed above. A special use of methyl violet may be mentioned here, viz. its use as a blueing agent after wool has been scoured or bleached. A minute percentage is used in order to correct any yellow tone of the wool, and thus greatly improve the colour of the wool: this is termed in some instances a "false bleach." This operation is usually carried out in a soap bath. The small quantity of colour—perfectly dissolved, spirit sometimes being used as the solvent—is added to the soap bath: the bath well stirred, and if any scum appears on the surface this must be removed before the goods are entered, otherwise there is a danger of flecky results being obtained.

Cotton.—The Basic Dyestuffs may be applied by several methods, viz.:—

(*a*) On a Turkey red oil mordant.

(*b*) With alum and soda ash in a single bath.

(*c*) On a tannin mordant.

Methods (*a*) and (*b*) may be dismissed in very few words, because they are of very limited application, owing to the shades rubbing very badly and being very loose to washing: brilliancy is their only recommendation.

Method (*a*).—The cotton is mordanted with Turkey red oil, wrung out and dried. The operation is repeated once or twice. The cotton may also be worked for 20 minutes at 104° F. (40° C.) in a bath made up of 1 part Turkey red oil to every 10 parts of water, wrung out and dried: it is then worked for half an hour at 120° F. (50° C.) in a bath containing 1 lb. aluminium acetate 77° Tw. to every 4 gallons of water. Wash well and dye as detailed under method (*c*).

Method (*b*).—The boiled-out cotton is entered into a bath at 195° F. (90° C.), charged with the requisite amount of colour, 10 lbs. of alum and $1\frac{1}{2}$ lbs. soda ash, steam is shut off, the cotton worked to shade and dried without rinsing. The bath is not exhausted, and should be kept up for subsequent lots, when only half the quantity of colour and assistant will be required. It will be recognized that this is not really a dyeing operation, but consists of merely painting the colour on the fibre.

Method (*c*).—The method of dyeing on a tannin mordant is at once the commonest and most effective method of applying the Basic Dyestuffs to cotton. Owing to cotton having no affinity for them, the lack of acid groups is overcome by mordanting the cotton with tannic acid, which supplies the necessary groups. The method of application is a long and tedious one, entailing much labour, so that it is not popular with dyers, but is avoided whenever possible.

Mordanting.—Tannic acid is used in the form of tannic acid, sumach or myrabolans, the strength of the two latter products varying considerably; from two to four times as much, according to the quality, is required compared with tannic acid. It is not advisable to use the two latter qualities for pale shades, owing to the natural colour of the products, unless the extracts have been specially decolorized. Experiments have shown that tannic acid is absorbed most readily by cotton about 104° F. (40° C.). One would naturally think, therefore, that the tannin mordant baths would be worked at this temperature. Practice, however, demands that the material to be mordanted should be entered into the boiling dyebath in order to ensure the goods being thoroughly penetrated with the tannin. It would be obviously absurd to enter a tightly twisted yarn into a tannin bath at 104° F. (40° C.), because the mordant would then never get into the centre of the yarn, with the result that it would only be subsequently surface dyed. Owing to iron reacting with tannic acid to form inks, the presence of iron in the water, or iron in the construction of the bath or steampipe, must be rigorously avoided. The ink-coloured compound would naturally detract from the brilliancy of the shade. Wooden vessels fitted with copper steampipes are commonly used.

Great care must be exercised in the amount of tannic acid used, because too little mordant does not exhaust the dyebath, whilst excess of mordant, in addition to being a waste of material, causes the colour to rush on the fibre, with consequently uneven results: moreover, excess of tannin causes the resulting shade to be dull and lifeless. It is always advisable, therefore, to determine by experimental dyetests the amount of tannic acid requisite for given colours in given percentages.

The following table indicates the average amounts required:—

Percentage of Colour.	Percentage of Tannin.	Percentage of Tartar Emetic.
0·1 per cent.	½ per cent.	¼ per cent.
¼ "	1 "	½ "
½ "	1½ "	¾ "
1 "	3 "	1½ "
1½ "	5 "	2½ "
2 "	8 "	4 "

Mercerised cotton and artificial silk, owing to their greater affinity as compared with ordinary cotton, may be dyed with less amounts.

The method of procedure is as follows:—the material is entered into a boiling bath, charged with the requisite amount of tannin and worked 10–20 minutes, in order to ensure the material being thoroughly penetrated. Steam is shut off, the material immersed under the liquor and allowed to steep overnight. Next morning the material is lifted out, wrung out evenly, then fixed without washing as detailed below.

Too much stress cannot be laid upon the necessity of the material being evenly wrung out, because if this is not efficiently done the final dyeing result is bound to be uneven, despite the most careful working in the later stages. It is obviously not possible to mordant cotton pieces in this manner. They are usually mordanted on a padding machine or in a jigger. After the pieces have been thoroughly impregnated with the tannin solution, they are batched on a roller and allowed to stand 1–2 hours before being fixed. The mordanting bath is not exhausted, so that it may be kept and replenished for subsequent lots with four-fifths of the original amount of tannin used.

No time should be lost in fixing the material, because the tannin drains to the lower portions of yarn hanging on sticks; uneven results will ensue, because more tannin will be deposited on the lower portion of the yarn. Pieces batched on rollers should not be allowed to be for long in one position, but the position of the roller should be altered so that there is no possibility of the draining of the liquor to the bottom half of the piece.

Mordanted material should never be put into work unless it can be carried right through to the end of the fixing without leaving the material lying about, say, during the dinner hour, because if it is so left about uneven results are inevitable. I have investigated more than one case where bad results have been caused by throwing yarn on top of the bath and allowing it to drain during the dinner hour without wringing the yarn out. Once the tannin has been fixed there is not the same necessity for these precautions, though the quicker the mordanted material is dyed the better the results obtained, because the least trace of iron—even from the condensed steam off the roof of the dyehouse—will cause a dark mark to appear on the cotton. If goods do get so stained with iron, the stains may easily be removed by working the material in a dilute solution of oxalic or sulphuric acid.

Sometimes uneven results in dyeing are caused by allowing the mordanted material to lie about before dyeing and decomposition of the mordant has taken place: the best remedy in such a case is to remove as much of the mordant as possible with hot dilute sulphuric acid, and then mordant again. If the material cannot be immediately dyed after mordanting, then it should be covered with a damp cloth.

Fixing.—The object of this process is to fix the tannin upon the cotton in an insoluble form. Cotton treated with tannin alone may be dyed with Basic Dyestuffs, but the results are not as fast, particularly to washing, as those dyed on cotton on which the tannin has been fixed. This is due to the fact that excess of tannin can dissolve the Tannin-Basic Dyestuff lake, whilst tannin which is fixed in an insoluble form cannot dissolve the lake, though it is quite capable of forming a lake with Basic Dyestuff. The result is that in actual practice the tannin is always fixed on the yarn. For this purpose antimony, tin, aluminium and iron salts are all used, but the most commonly used salt is tartar emetic (potassium antimony tartrate, $KSbOC_4H_4O_6$), because antimony gives the fastest results to washing.

Fixing is carried out by working the evenly wrung tannin impregnated material in a cold bath for half an hour. The amount of tartar emetic used is exactly half the amount of tannic acid used. The material is then thoroughly washed to remove all loosely adhering particles of tannate of antimony, which would cause the colour to rub. A light soaping is sometimes given at this stage to ensure the minimum amount of rubbing.

Iron salts are used because they are much cheaper than tartar emetic, and because their use is most helpful in some cases in obtaining the desired shade in an economical way. Iron salts combined with tannic acid produce an ink-coloured compound, which enables a considerable economy of colour to be effected when dyeing dark shades. If a dark navy blue is required it would be absurd to start with methylene blue on a tannin-tartar emetic mordant, and flatten it with chrysoidine. It is much cheaper to dye with methylene blue on the ink-coloured tannin-iron mordant. At the same time, however, it must be remembered that these iron-fixed shades are not fast to acids. Acids decompose the tannin-iron lake, so that the use of iron salts is barred, if the cotton will subsequently come into contact with acid.

When using iron salts for fixing, the fixing bath is charged with 3–5 per cent. ferrous sulphate (copperas), or the bath is charged with iron liquor or nitrate of iron (really a mixture of ferric sulphates-nitrates) to stand at 2–4° Tw. according to the amount of tannic acid used: the cotton is next passed through a weak bath of lime-water and thoroughly rinsed. Tin is used in the form of stannic chloride and aluminium in the form of aluminium acetate. The fixing baths are not exhausted, and may be used continuously by replenishing with four-fifths of the original quantity taken.

The fixing bath gradually becomes acid when continuously used: this acidity should be corrected from time to time with soda, which should be carefully added till the bath begins to turn cloudy.

Dyeing.—The addition of acid or acid-reacting salts to the dyebath has a considerable effect in the rate of dyeing of the Basic Dyestuffs. It is, therefore, customary to use acetic acid or alum in the dyebath in order to retard the rate of dyeing and so facilitate the obtaining of level shades coupled with better penetration. Moreover, in order to ensure that the cotton is impregnated with the acid before the dyestuff, it is advisable when dyeing shades which prove difficult to dye level to work the cotton ten minutes in the cold dyebath, charged with only 1–5 per cent. alum or acetic acid, according to the depth of the shade to be dyed. After which one-third of the colour solution is added and the cotton worked ¼ hour cold; half of the remaining colour solution is now added and the cotton again worked ¼ hour; finally the remainder of the colour solution is added and the bath gradually raised to 140° F. (60° C.), in ½ hour after which the cotton is washed off and dried.

Remordanting or Backtanning.—This process consists in again passing the cotton after dyeing through the old mordanting and fixing baths without replenishing them. The cotton is worked in the cold tannin bath for ½ hour, wrung out or hydroextracted, worked ¼ hour in the cold fixing bath, then finally well washed off.

This additional treatment further lengthens an already long dyeing process, but it has the advantage of considerably improving the fastness of the colours to milling and cross-dyeing, but it has the disadvantage of dulling the brilliancy of the shade, so that when a shade has to be back-tanned, allowance must be made for this dulling effect when dyeing the shade.

Despite the length of the process it is, however, employed for shades which have to withstand a severe milling or cross-dyeing, *e.g.* the bright shades which are to be subsequently used as checking threads in cloth, which will be heavily milled or subsequently cross-dyed; whilst all Basic Dyestuffs are more or less improved by back-tanning, it is most advantageous with the following colours :—

Auramine O.
Brilliant green crystals.
Malachite green crystals.
Methylene blue.
Saffranine.
Victoria blue.

Artificial Silk.—Owing to the fragile nature of artificial silk, the Direct Cotton Dyestuffs are used whenever possible, because their application involves the minimum amount of handling, whereas it has been seen above that the Basic Dyestuffs involve the maximum amount of handling. However, their use is compulsory when very brilliant shades are required. Nitro-cellulose artificial silk may be dyed with Basic Dyestuffs without any previous mordanting, but the other varieties have to be tannin-mordanted, which is carried out as follows :—

A bath is charged with 2–5 per cent. tannin and 1 per cent. hydrochloric acid—according to the depth of shade to be dyed—and the material immersed in this bath for 2 hours at 104° F. (40° C.). The material is then wrapped in cotton bagging and hydroextracted, after which it is worked in a fresh bath charged wth 1–2½ per cent. tartar emetic for ½ hour cold. Wash well, then proceed with the dyeing as detailed for cotton.

Jute.—For the purposes of dyeing with Basic Dyestuffs coir fibre, piassava, sisal, straw and wood chip may be classified with jute. Owing to the fact that tannin bodies enter into the constitution of jute the Basic Dyestuffs have a strong affinity for it without any previous mordanting. This class of dyestuffs is of prime importance in the dyeing of jute, because being a very cheap fibre cheapness coupled with brilliancy of shade is a governing feature in its dyeing, whilst fastness is of secondary importance in the classes of jute goods for which the Basic Dyestuffs are used. The dyeing of jute on the big scale is carried out in a quick and simple manner, because the prices paid for the dyeing do not admit of any undue amount of labour and time being spent on it. The Basic Dyestuffs—always with the exception of auramine, which decomposes above 160° F. (70° C.)—are dyed for 20–30 minutes at the boil, with the addition of alum or acetic acid. It may be said that alum gives the fuller shade, but that the shades dyed with acetic acid are faster to rubbing. The carrying out of the above method is not, however, as simple as it may appear, because it is essential that the jute should be well penetrated—or "hearted" as the trade terms it—for many classes of work, especially yarn, which is subsequently to be made into pile goods, for which effect the yarn has to be cut. It is a defect of some of the Basic Dyestuffs that they do not heart the jute at all well, notably methyl violet and Bismarck brown. These two colours should, therefore, be avoided in all compound shades. Chrysoidine should always be given the preference over Bismarck brown in compound shades, because the former "hearts" much better than the latter. The effect of this may very easily be seen by dyeing a bronze green shade in one case with auramine, chrysoidine and malachite green, and in other case with auramine, Bismarck brown and malachite green. The shade dyed with chrysoidine will be much better penetrated than the one dyed with Bismarck brown, whereas the latter will also be flecky, because Bismarck brown does not mix well with the other colours. The same applies in case of jute blacks, which are usually composite colours. A satisfactory black may be obtained by a combination of magenta, chrysoidine, and malachite green, whilst unsatisfactory ones will be obtained by a combination of methyl violet, Bismarck brown and malachite green.

Paper.—The Basic Dyestuffs find a large application in the dyeing of paper, especially auramine, saffranine, magenta, methyl violet, and malachite green, all of which colours have become standardized in the paper trade. They are simply dyed by adding the colour solution to the beater and beating the pulp up till it is uniformly dyed.

Leather.—The Basic Dyestuffs are largely used in the dyeing of leather, but their use is more restricted than it otherwise would be owing to the fact that they, as a class, show up any defects in the leather in a much more marked degree than the Acid Dyestuffs. It naturally follows that the latter are therefore given the preference by leather dyers whenever the desired shade can be obtained with them.

Vegetable-tanned leather has a direct affinity for the Basic Dyestuffs due to the tannin bodies used in the tanning process: chrome-tanned leather, on the other hand, must be given a preliminary treatment with sumac—1–2 lbs. per dozen skins—for ½ hour at 120° F. (50° C.). Excess of sumac should be avoided, because it lessens the elasticity and strength of the leather.

When dyeing the skins should first be worked a short time with acetic acid only (1 lb. per 10 gallons water), the colour solution being added in several lots at intervals to the dyebath: this tends to prevent the colour from striking rapidly and unevenly.

Phosphines are amongst the most popular Basic Dyestuffs for leather and are used as the basis of most tan shades.

GENERAL NOTES

The Basic Dyestuffs are used for topping both Direct Cotton and Sulphur Dyestuffs in order to get brighter shades than are possible with the latter dyestuffs alone: the methods employed will be found detailed in the respective sections dealing with these two classes of dyestuffs.

Basic Dyestuffs cannot be mixed in the same bath with Direct Cotton, Acid and Sulphur Dyestuffs because precipitation takes place.

Basic Dyestuffs are largely consumed in the ink trade, for hectrographic inks, typewriter ribbons, copying paper and pencils, etc.

SECTION III—ACID DYESTUFFS

THE Acid Dyestuffs include the following distinct chemical groups :—

Nitro Dyestuffs	Naphthol Yellow.
Mono Azo Dyestuffs ..	Roccelline.
Disazo Dyestuffs ..	Croceine Scarlet.
Nitroso Dyestuffs ..	Naphthol Green.
Triphenylmethane Dyestuffs	Acid Magenta.
Xanthene Dyestuffs ..	Fast Acid Violet A2R.
Anthracene Dyestuffs ..	Alizarine Delphinol SE.
Azine Dyestuffs	Azocarmine.
Quinoline Dyestuffs ..	Quinoline Yellow.

Despite the variety of the colours from the chemical point of view they are all one class from the dyeing point of view in that they require to be dyed from an acid dye-bath, hence the name "Acid" Dyestuffs. They place at the dyer's disposal a most comprehensive range of colours with the most varying degrees of fastness to light, milling, stoving, etc. For example, soluble blue is extremely fugitive to light, alizarine delphinol SE is extremely fast : acid magenta possesses no fastness to milling, whilst Coomassie navy blue is very fast to milling. Roccelline is a very bad levelling colour, XL fuchsine 6B is a very easy levelling colour.

The Acid Dyestuffs are usually put on the market in the form of the sodium salt of their sulphonic acid, though some are put on the market as the lime salt, *e.g.* patent blue. It was formerly usually accepted that the procedure of dyeing was as follows. The acid used combined with the sodium of the sulphonic acid group of the dyestuff, liberating the free colour acid, which then combined with the base of the wool substance, forming a coloured compound, which represents the shade dyed. This idea was first shaken by Knecht (*J. S. D. C.* 1888, p. 107), who showed that if wool is first boiled with 5–10 per cent. sulphuric acid, and is then treated with water till no more acid is extracted, it dyes a fuller shade in a neutral bath with an acid dyestuff than is dyed with the same acid dyestuffs in the ordinary way with acid in the dyebath. Hallitt (*J. S. D. C.* 1899, p. 30) showed that the free colour acids of acid dyestuffs do not dye wool in a neutral dyebath better than the alkali salts of the dyestuffs; whereas if the above idea held good they should do so. Finally, Fort has made many contributions on this subject, which he has summarized (*J. S. D. C.* 1916, p. 33), to which the reader is referred for full details. He concludes that the wool base forms an additive salt with sulphuric acid, and that the process of dyeing wool with an acid dyestuff may be expressed by the following equation:

$$\text{Wool Base } H_2SO_4 + \text{Colour Acid Na Salt} \rightleftarrows \text{Wool Base Colour Acid} + Na_2SO_4$$

The reaction is reversible, which shows why Glauber's salt is used as a levelling agent because it retards the rate of dyeing, whilst it also explains the reason why a boiling concentrated Glauber's salt bath will more or less strip most Acid Dyestuffs from the fibre. To quote Fort's own words, "Commercial dyeing of Acid Dyestuffs is mainly dependent on the use of a free acid in conjunction with the dye, and the acid thus rendered to dyeing is dependent on the chemical reaction between dye and the acid fibre compound formed initially and not as hitherto commonly supposed as a process of liberation of free colour acid in the bath." The application of the Acid Dyestuffs is so simple that they are naturally of large consumption, since dyers rightly use them wherever possible. They are largely used for the dyeing of silk and the following branches of wool dyeing: gentlemen's suitings, ladies' dress goods, knitting and hosiery yarns, carpets, and hat dyeing. They find a limited application in the dyeing—or rather painting—of cotton pieces. Certain types find very extended application in jute, paper, and leather.

APPLICATION.

Dissolving.—Stir the colour into a perfectly smooth paste with cold water, then dissolve by pouring boiling water over it whilst stirring. Amongst the Acid Dyestuffs the solubility of individual members varies considerably, so that the above instructions are superfluous for those which are freely soluble, at the same time it is advisable as a matter of dyehouse routine to stir every colour into a perfectly smooth paste with cold water before adding boiling water. Such procedure will prevent the material being flecked, due to undissolved colour getting unobserved into the dyebath.

Assistants used.—Glauber's salt is practically universally used with Acid Dyestuffs because it retards the rate of dyeing and thus helps to prevent the colour rushing on to the fibre, it therefore fills the rôle of a levelling agent.

The acids which are commonly used are sulphuric, formic and acetic acids, whilst bisulphate of soda (nitre cake) has not been used much in this country prior to the war, but stress of war conditions has forced its use, though dyers are loud in their complaints of the inconvenience caused by its storing and dissolving. The most convenient way I have seen of handling this product was to place it in a lead-lined tank into which steam was blown from four sides. The resulting liquor was drawn off from the bottom by a tap and yielded a 12 per cent. solution of sulphuric acid.

Of the above three acids sulphuric acid is most commonly used owing to its cheapness. Formic acid is a comparatively new acid for wool-dyeing and is of practically equal power to sulphuric acid, but has the advantage that its action on any cotton present is not so severe as that of sulphuric acid. It is, therefore, given the preference in dyeing woollen pieces containing cotton effect threads. Acetic acid is considerably weaker in acidity and is always used when it is necessary to dye colour in a weakly acid bath or in the dyeing of goods which are difficult to penetrate: in other words, dyeing proceeds much slower when acetic acid is used.

Bisulphate of soda (nitre cake) when dissolved in water resolves itself into Glauber's salt and sulphuric acid, so that it is quite suitable for use in dyeing acid dyestuffs. It may be averaged as containing 25 per cent. sulphuric acid.

It has always been largely used in continental practice, but has only been largely used in Great Britain since the war.

DYEING.

Silk.—Dye in a boiled-off liquor bath broken with sulphuric, formic or acetic acid. Start the bath lukewarm, raise gradually to 190°–200° F. (90°–95° C.), and dye ½–1 hour at this temperature. It is not advisable to actually boil the dyebath for silk, because many acid dyestuffs begin to boil off the fibre at the actual boil. Again, certain dyestuffs, such as roccelline, have so pronounced an affinity for the silk that they can be dyed equally satisfactorily at a lower temperature than indicated above. The lower the temperature employed, the better is the natural lustre of the silk preserved. After dyeing rinse and brighten in weakly acidulated water. The special methods for certain dyestuffs given under " Wool " are equally applicable to silk.

It has become an increasingly common practice to weight silk by means of stannic chloride and sodium phosphate in order to reduce the price. This is very liable to cause trouble to the dyer in several ways. If the weighting is not carefully done, the tin salts may be precipitated unevenly on the fibre, which it is then subsequently impossible to dye level.

If weighted silk is stored any length of time the weighting is liable to decompose and it is impossible to dye such silk level.

Finally, many acid dyestuffs which will dye unweighted silk satisfactorily possesses no affinity for the weighted silk due to the tin salt resisting the dyestuff.

It will be useful to include here two methods of distinguishing the weighted from the unweighted silk. A simple test to distinguish between unweighted and tin-weighted silk is to boil some with a little alizarine orange paste. If the silk is tin-weighted the silk will be coloured bright orange, owing to the combination of the alizarine orange with the tin on the fibre. An unweighted silk will only be stained a dull bluish pink.

Another largely used test is to boil the silk with logwood and acetic acid. Tin-weighted silk is coloured violet, due to the formation of the logwood-tin lake; unweighted silk is stained red, *i.e.* the colour of the logwood and acetic acid solution.

Wool.—In dyeing the average acid dyestuff the bath, in which there is about one foot of water, is charged with the requisite colour and Glauber's salt. This is boiled for ten minutes, then the bath is thoroughly stirred with a rake. Another method is to put the colour in a cotton bag and boil the bag till all the colour is dissolved. The material is entered, worked ten minutes, steam turned on, and the bath brought to the boil in ½ hour and dyeing continued at the boil for ½–1 hour. The amount of Glauber's salt and sulphuric acid used varies with the depth of shade, thus:—

Colour.		Glauber's Salt.	Sulphuric Acid.
½ per cent.		10 per cent.	1 per cent.
1 ,,		10 ,,	2 ,,
2 ,,		20 ,,	3 ,,
2 ,,		25 ,,	4 ,,
8 ,,	(Blacks)	25 ,,	5 ,,

Several modifications of the above method may be made, which depend on the class of the material being dyed and the nature of the dyestuff employed. The following modifications may be made and their adoption in suitable cases must be left to the discretion and experience of the individual dyer. If the colour belongs to the easy-levelling class the material may be entered into the bath at a much higher temperature, and no time need be wasted in raising the bath to the boil. If a colour shows a tendency to rush too quickly on to the fibre, the amount of Glauber's salt should be increased to 40–50 per cent. and acetic acid substituted for sulphuric acid, which prevents the colour striking too rapidly; a little sulphuric acid may be added towards the end of the dyeing if the bath cannot be sufficiently exhausted with acetic acid. Another way is to start the dyebath with the colour and Glauber's salt only, and to gradually make the bath acid by adding the acid, well diluted with water, in small quantities at intervals after the material has been thoroughly saturated with the colour solution.

If difficulty is experienced in getting the colour to penetrate thick cloths or tightly twisted yarns, and the above modifications do not give the desired result, then use is made of acetate of ammonia. Acetate of ammonia may be made by mixing four parts ammonia (24 per cent.) with 10 parts acetic acid (30 per cent.); this will be slightly alkaline to litmus, which is no disadvantage when it is being used for dyeing. As the bath gets hot the ammonium acetate splits up into ammonia (which boils away) and acetic acid. The result is that the bath becomes slowly acidified, so that the dyeing proceeds regularly and slowly and the dyestuff is prevented from rushing on to the surface of the material. When using acetate of ammonia, it will usually be found necessary to add acetic or even sulphuric acid towards the end of the dyeing in order to exhaust the bath. Woollen pieces containing cotton or artificial silk effects which have to be left white or, if coloured, unstained require to be dyed in a strongly acid bath. Formic acid is often used for this purpose because it has not the same tendering effect on the cotton and artificial silk as sulphuric acid. Such pieces should be washed off immediately after dyeing and no time should be lost in drying them; if left lying about in the wet state, the wool colour is very liable to bleed on to the effects and stain them, although they were perfectly clean when they came out of the dyebath.

The alkali blues give very fine bright shades on wool and silk; they are still great favourites for the latter fibre. They require to be dyed in the following manner: dye at 195° F. (90° C.) for ½ hour with the addition of 1–4 per cent. borax or 1–3 per cent. soda ash, wash and develop for ½–¾ hour at 100°–140° F. (40°–60° C.) in a bath containing

1–4 per cent. sulphuric acid according to the depth of shade being dyed. In the dyebath the shade is very weakly blue, but develops up to a full blue in the acid-developing bath. This method of dyeing has to be adopted because sulphuric acid precipitates alkali blue, due to the insolubility of the free colour acid in water.

The sulphoncyanines and allied dyestuffs have won for themselves a most important place in wool-dyeing, due to their fastness to light and milling, but their adoption by the dyeing trade was very slow, due to the many difficulties encountered in their application. This is now thoroughly understood, with the result that these dyestuffs have become standardized for certain classes of goods, especially piece dyed goods.

The following three points must be carefully attended to in order to get successful results :—

1. The wool must be perfectly scoured and free from grease; this is, of course, true for all wool colours, but sulphoncyanines are peculiarly sensitive to any grease or soap residues.

2. Sulphoncyanines are sensitive to reducing agents, *e.g.* stoving with sulphur dioxide reduces them to brown. This brown reduction can take place in the dyebath, especially if the bottom of the cistern is covered with large perforated iron plates. I have come across such instances of the wool coming out brown instead of blue due to this cause. Fortunately the prevention of this reaction is very simple. Sulphoncyanines are unaffected by boiling with bichrome, so it is always advisable to dye with the addition of ½–1 per cent. bichrome, which immediately kills any reducing agent, which may be generated in the bath. It will also be found that this addition of bichrome yields brighter shades than if no bichrome is added. This is particularly noticeable the longer the dyeing is continued. It is due to the fact that a certain amount of this reduced brown colour is produced in each dyeing which is sufficient in quantity to flatten the shade. Bichrome prevents the formation of even this small quantity and so yields brighter shades.

3. The sulphoncyanines have a very marked affinity for wool and silk, so that they cannot be dyed level in the normal method of application used for Acid Dyestuffs.

The above explanation makes clear why it is necessary to dye the sulphoncyanines as follows :—

The dyebath is charged with the requisite amount of colour, ½–1 per cent. bichrome and 10–25 per cent. Glauber's salt. The material is entered cold and the bath carefully raised to the boil in the course of ¾–1 hour. It is not necessary to have the bath boiling vigorously, but just simmering. The bath is now usually well exhausted, steam is shut off, and 2–5 per cent. acetic acid, well diluted with water, is added, steam put on again, and dyeing continued for ½ hour at the boil. The opinion of dyers is divided on the question of the addition of acetic acid. Those who do not use acetic acid argue correctly that the danger of uneven results is much reduced if no acid is added; on the other hand, it is agreed that the shade is fuller, though less bloomy, if acetic acid is added. In dyeing loose wool, therefore, on which absolutely level results are not of such moment, acetic acid should be added; if dyeing yarn or piece the use of acetic acid must be left to the discretion of the dyer, but it is safer to omit it even at the expense of some loss of colour.

All wool which is to be dyed with sulphoncyanines should be carefully scoured, because if not uneven results will be sure to ensue. Dirty pieces, or pieces which have been stored for some time, should be chromed before dyeing.

Another method which is advisable for dyers to use who have reason to doubt pieces coming to them is to run the pieces through a weak ammonia bath at 140° F. (60° C.). Take 1 quart of ammonia for 50 lbs. material, This will remove any soap residues on the pieces.

The dyeing of wool may take place at four different stages of its manufacture, viz. :—

1. Loose Wool.
2. Slubbing.
3. Yarn.
4. Piece.

The particular stage in which the wool is dyed depends upon the quality and class of goods into which it is going to be manufactured, thus it is essential for goods showing a mixture effect that the wool be dyed in the form of loose wool or slubbing, and the mixture effect be obtained by blending. Wool for carpets is universally dyed in the form of yarn, as is a large proportion of knitting yarn. The majority of ladies' goods and the cheaper qualities of men's goods, as well as blacks and blues in the best qualities, are dyed in the piece. Dyeing in the piece is the cheapest method and is adopted whenever circumstances will permit. Dyeing in the form of loose wool or slubbing is the most expensive, but gives the best results, since the individual fibres are more thoroughly penetrated than is mechanically possible with wool in the form of yarn or piece.

In whatever form the wool is dyed it is essential in order to obtain fast, clean and level results, that the wool be efficiently scoured, so that the colour may not be prevented by grease from penetrating the fibre. Many cases of unlevel dyeing prove on examination to be due to inefficient scouring or to the precipitation of lime soaps on the wool, due to the presence of lime salts in the water or to the application of soap to carbonized goods before the acid had been thoroughly neutralized by a preliminary treatment with alkali alone.—Lime soaps may be removed by treatment with spirits of salts, since this liberates the soap and combines with the lime to form calcium chloride, which may be easily removed by washing. The liberated soap is removed in a subsequent bath with warm weak ammonia. Sulphuric acid must not be used in place of spirits of salts, since this combines with the lime to form sulphate of lime, which is very insoluble and cannot, therefore, be thoroughly removed by washing.

Loose wool is dyed in open vats of iron or wood, or in one of the many forms of loose-wool-dyeing machines, into the merits of which it is not the author's province to enter. Slubbing is either dyed in the ball form in suitably constructed machines or wound into hanks and dyed in an ordinary cistern or hank-dyeing machine.

Yarn is dyed in a suitably constructed machine or in the open cistern, in some of which the width allows for 2 lbs. on each stick, whilst others permit of 4 lbs. on 1 stick. Arms are frequently arranged over the cistern, so that when it is necessary to lift the yarn the sticks may be lifted straight on to these arms. The height of the arms is so arranged that the yarn clears the dyeliquor by at least 6 inches.

In piece dyeing the winch machine is practically the only one at present used; whenever possible two methods of driving should be available; first, a drive from the mill shafting, which is the more economical; and secondly, a donkey engine, so that the dyeing may be continued when the mill engine is stopped. For each of these drives a reversing gear should be fitted, so that the winch may be turned in either direction in case the pieces become entangled, etc. Pieces having tightly-woven lists which curl badly should be sewn together at intervals of 3 to 6 inches. Dark lists can usually be avoided by letting the pieces run in rope form and changing the position of the folds by occasional poling. When dyeing pieces it is absolutely essential in order to ensure level results that all pieces be properly scoured and that all scouring agents be thoroughly removed; if the pieces are not to be dyed immediately after washing off they should be always folded so that the tail-end of the piece completely envelopes the whole.

It is always advisable to tenter the pieces, if they have to stand some time before dyeing, because in the wet state the wool has a greater tendency to be acted upon by the atmosphere and thus give rise to unevenness and stripiness, since the affinity of wool which has been exposed to air and light is quite different from wool which has not been so exposed. This difference is only apparent after dyeing. When the pieces are dyed to the required shade, shut off steam and run straight into a tank of cold water, rinse well and cuttle again, taking the precaution to wrap up in the tail end of the piece, unless it is going to be put immediately on the machine. Carbonizing is a constant source of trouble if care is not exercised in carrying it out. It has for its object the removal of vegetable impurities from the wool. Wool is usually carbonized with sulphuric acid, whereas rags for shoddy manufacture are usually carbonized with hydrochloric acid.

Wool is carbonized in the form of loose wool or pieces. The wool is saturated with sulphuric acid 5° Tw., then hydro-extracted and dried at 180° F. (80° C.). This treatment disintegrates all vegetable matter. The two points which must be watched from the dyer's point of view, particularly with pieces, are :—

1. Wool saturated with acid if exposed to light is so changed that it refuses to take the dyestuff. If, therefore, a piece is so exposed these exposed places refuse to take the dye and the piece is ruined.

2. No soap must be allowed to come into contact with carbonized wool until the wool has been thoroughly neutralized with soda ash. If such a thing does happen then the soap is decomposed by the acid into free fatty acids, which stick to the cloth and play havoc in the subsequent dyeing.

Correction of Uneven or Wrong Shades.—Material dyed with acid colours which is slightly uneven may often be corrected by boiling in clean water with a large percentage of Glauber's salt, if necessary with some grey material to absorb some of the colour. If this is not effective, strip some of the colour off with hot ammonia, then re-dye on the colour by gradually acidifying the bath. If this is not sufficiently effective the colour must be stripped down with hydrosulphite.

Jute.—A limited number of Acid Dyestuffs are of the greatest importance for jute and are largely used. They possess several advantages over the Basic Dyestuffs because they dye on more slowly and therefore penetrate or "heart" the jute fibre better. They are also faster to rubbing, whilst they are also much faster to light. The following Acid Dyestuffs are commonly used for jute :—

Indian yellow.
Acid scarlets.
Soluble blues.
Fast red.
Acid green.
Naphthalene black 12B.
Orange IV., II.

Dyeing is carried out at the boil with the addition of Glauber's salt and acetic acid, or with alum. In general it may be said that acetic acid gives cleaner shades, but alum gives the fuller shades. The above remarks apply equally to coir fibre, piassava, sisal, straw, wood chip.

SECTION IV.—TRUE ALIZARINE AND OTHER MORDANT DYESTUFFS

THOUGH true alizarine dyestuffs are quite distinct chemically from the other mordant dyestuffs their methods of application overlap sufficiently closely to justify their inclusion in the same section. The methods of application detailed hereafter apply to the following groups of mordant dyestuffs :

Anthracene Dyestuffs.	Alizarine.
Monoazo Dyestuffs.	Mordant Yellow O.
Disazo Dyestuffs.	Diamond Black F.
Oxazine Dyestuffs.	Gallocyanine.
Triphenylmethane Dyestuffs.	Chrome Violet.
Nitroso Dyestuffs.	Gambine.
Oxyquinone Dyestuffs.	Alizarine Black.
Xanthene Dyestuffs.	Coerulein.

In the naming of colours which may be applied in the same way as true alizarine dyestuffs there has been a regrettable looseness which may mislead those who are not familiar with the constitution of the colours concerned. For instance, anybody seeing anthracene yellow BN for the first time would naturally conclude that it bore at least some chemical relationship to anthracene, whereas it has none, but it is a monoazo dyestuff derived by combining salicylic acid on diazotized B naphthylamine mono sulphonic acid. Again, acid alizarine brown would lead the uninitiated to conclude that it belonged to the alizarine class, whereas it has no chemical relationship whatsoever to alizarine, but is made by combining meta phenylene diamine on ortho-amido-phenol-mono-sulphonic acid. However, they may all be treated together from a dyeing point of view.

From another point of view the true alizarine dyestuffs sharply differentiate themselves from other mordant dyestuffs, in that true alizarine dyestuffs will not dye wool without the aid of a mordant, whereas the other mordant dyestuffs will dye wool a more or less deep but not fast colour without the help of a mordant.

This class of dyestuffs is applied to silk, wool and cotton and yield some of the fastest shades obtainable on these fibres: they are consequently used for the best classes of work on the respective fibres. For example, Turkey red (alizarine on alum mordant) has remained for years without a rival as the fastest obtainable red on vegetable fibres. Of recent years para red (paranitraniline coupled with B naphthol) has displaced it—more particularly on pieces—not on the score of fastness, but on the score of cheapness and ease of application, thus enabling increased production. It is safe to say that vat red will sooner or later also rival it. On wool the shades obtained are so much superior in fastness to light that they have displaced all the old dyewoods with the exception of logwood—which holds its own, due to its beauty of shade and cheapness—and fustic, which holds its place as a yellow owing to yellows being the weakest member of this series—there being no true alizarine yellow. With the increasing adoption of the single-bath methods of dyeing, both logwood and fustic were—until the war revived them—losing ground. On silk shades of perfect fastness to boiling soap are obtained: shades which cannot be obtained by any other method of dyeing. The mordant dyestuffs are put on the market in the form of pastes and powders. Some of the former are delivered in the form of their bisulphite compounds, particularly alizarine blues. The bisulphite compounds of the alizarine dyestuffs are soluble as compared with the alizarine dyestuff itself, which is insoluble. On warming to 160° F. (70° C.) the bisulphite compound splits up and the insoluble alizarine dyestuff is precipitated. This entails special precautions in dyeing these compounds, which are detailed later.

APPLICATION.

Dissolving.—Pastes are stirred into a perfectly smooth paste with cold water, then added to the dyebath through a fine hair sieve in order to catch any lumps which would give trouble if they got into the dyebath undetected. Powders are dissolved by the methods already detailed in Section III.

Cotton.—The main use of the alizarine dyestuffs in the dyeing of cotton is alizarine on an alum mordant to produce the well-known Turkey red, but in calico printing their application is much more widespread.

The dyeing of Turkey red on cotton is a section of the dyeing trade which has bcome concentrated in very few hands in the countries in which it is dyed. The author makes no claim to any experience in this special line of dyeing. The two sources for which I am indebted for the following details are "The Manual of Dyeing," Knecht, Rawson and Lowenthal; and "Turkisch Rot and Seine Concurrenten," by F. Felsen. Previous to the introduction of synthetic alizarine Turkey red was dyed with madder. It is one of the oldest processes extant, and travelled from the East Indies to France via Persia, Armenia, Syria, to Turkey and Greece. 1790 is given as the probable date of its introduction to Great Britain at Glasgow, and the Vale of Leven is still the locality in which it is most largely dyed in Great Britain. The process as carried out in olden days lasted as long as four months, which has now been cut down to three days, though the fastness is not as good. Felsen states that the old Turkey-red process now takes eighteen days, as against five days for the new Turkey-red process. Turkey red as produced on the fibre is not a simple aluminium alizarine lake, but is a compound lake of aluminium and calcium with alizarine. The following are the processes involved in the production of what is termed old and new Turkey red. The distinction between these two processes is that in the old process the oil is rancid olive oil, whilst in the new process the oil used is sulphated castor oil. As can be noted from the number of operations, the second process is much cheaper than the first; at the same time, repeated washing tests show that the old process gives the faster colour, but it must not be thought the new Turkey red is not a satisfactory colour, because it is a very fast colour.

Turkey-red Dyeing Processes.

Old Process or Emulsion Process.—The process which serves for the production of the very fastest Turkey red on cotton yarns is conducted in the following manner :—

First Operation—Boiling.—The yarns are never bleached by chemicking (or treatment with chloride of lime solution), but simply freed from the naturally adhering fatty and resinous substances by "bowking"—*i.e.* boiling under pressure with alkaline liquors. The general method is to boil the yarn for four to five hours, under a pressure of 30 lbs., in a solution of caustic soda-lye of 1° Tw. Some use silicate or carbonate of soda or work in low pressure kiers; in these cases the boiling has to be continued for six to eight hours. When the yarn has been thoroughly cleaned in this way it is washed well with water, hydro-extracted, and dried in a stove at 120°–140° F. (50°–60° C.).

Second Operation—First Green Liquor.—The yarn is passed into the so-called first green liquor, which is prepared by mixing rancid olive oil with sodium carbonate and sheep or cow dung. The most suitable olive oil is that which forms the most perfect and permanent emulsion with the smallest quantity of sodium carbonate. For 100 lbs. of yarn the bath is made up with 15 lbs. of emulsive oil, 1½ to 2 lbs. of dung, 20 galls. of water, and so much of a concentrated solution of sodium carbonate as will bring the liquor to a specific gravity of 2° Tw. In this bath the yarn is thoroughly saturated with the emulsive liquor, at a temperature of about 100° F. (40° C.), for half a minute, and then wrung out evenly. This process, usually called tramping, is done by "tramping machines," which steep the single hanks into the liquors and often also wring out the hanks without much hard labour. After being well prepared the hanks are thrown out into heaps for the night; on the following morning they are exposed to the open air until they feel dry; and finally, they are placed in "stoves" heated to 140° F. (60° C.) for twelve hours (stoving). In some works which produce the very best kinds of Turkey red, as regards fastness to alkalies and to chlorine, the yarns are exposed in the open air for three or more days, and then they need not be placed in the stoves; while at present they are frequently brought straight into the stoves after having been piled up overnight. In this last case the steam given off in large quantities during the drying must be allowed to escape, as its retention causes the fibres to be tendered. During the prolonged exposure of the yarns in the open air the fibre is bleached by the sun, especially in the sunny Eastern countries; the slightly greater brilliancy of the Turkey reds which have been produced in the East is attributable to this action.

Third and Fourth Operations—Second and Third Green Liquors.—These consist of a second and third repetition of the second operation, the object being to increase the amount of oil in the fibre. The baths are prepared exactly as for the first green liquor, and the goods are steeped, exposed to the air, and stoved as before; but it is not necessary to pile them up to lie in heaps overnight.

Some of the alkali which is used in preparing the bath is liberated by the chemical transformation of the oil in the fibre and dissolves, during the second and third treatment, in the green liquor, which is absorbed by the yarn. The excess of this liquor, which is pressed out by the wringing of the hanks, if allowed to flow back into the tramping tank, would change the specific gravity of the bath, and as it is of importance that all the liquors should be maintained regularly of the same specific gravity, only the liquor which is expressed during the steeping in the first oil bath is allowed to run back into the tramping tank; that from the second and third oil baths is collected separately and used only after being reduced to its original specific gravity by dilution with water.

About 30 per cent. of oil of the weight of the yarn is used, but only a part of this is permanently fixed in the fibre.

Fifth, Sixth, Seventh and Eighth Operations—First, Second, Third and Fourth White Liquor Baths.—The yarn has been impregnated with oil, and the latter transformed into such a state by the hanging and stoving operations that it is not readily stripped by weak alkaline liquors. A part of the absorbed oil, however, has not become insoluble or adheres superficially to the fibre. This oil is removed by repeated treatments with alkali in order to avoid the formation of the "surface" colour, which is always disposed to rub and smear off.

The goods are tramped for this purpose four times in solution of sodium carbonate (2° Tw.), wrung out, hung up in the open air, and "stoved" as in the previous operations; a different bath is used each time. The oil which is stripped from the fibre forms an emulsion and imparts a white colour to the bath, hence the name white baths. The old white baths may be used for the preparation of fresh green liquors.

Ninth Operation—Steeping.—The yarn is steeped for a further purification in water at 130° F. (55° C.) for twenty-four hours, washed well and stoved at 140° F. (60° C.). If it still contains much unmodified oil a solution of sodium carbonate at ½° Tw. is used, the yarn steeped two hours in tepid water, washed and dried.

Tenth Operation—Sumaching or Galling.—An infusion is prepared of 12 lbs. of best leaf sumach for every 100 lbs. of yarn, and the cold solution is filtered and diluted to 1½° Tw. The yarn, while still warm from the stoving operation, is steeped for six hours in the solution at 120° F. (50° C.), and then hydro-extracted. It thus takes up a certain amount of tannic acid.

Eleventh Operation—Aluming or Mordanting.—Cake alum is dissolved in warm water and, when nearly cold, a cold solution of one-fourth its weight of soda crystals is added. Fifteen to twenty per cent. of red liquor, 16° Tw., and 0·5 to 0·7 per cent. tin crystals (of the weight of the alum) are often added to the liquor, but these additions are not essential. The addition of stannous chloride is made to prevent ferric oxide from entering into the colour lake and to introduce tin in some form into the colour, to make the shade more fiery. In this solution, which is brought to a specific gravity of 8° Tw. and kept at a temperature of 100°–120° F. (40°–50° C.), the yarn is steeped for twenty-four hours, then thoroughly washed and hydro-extracted. By this operation aluminium salts are formed, with the previously fixed oxyfatty acids and tannic acids.

The yarn, which is at last ready for dyeing, should now possess a deep yellowish tinge.

Twelfth Operation—Dyeing.—The goods are best dyed in wooden vats with closed steam coils of tinned copper. Iron vessels must be covered from time to time with a coating of insoluble iron tannate, by boiling out with a weak decoction of sumach; if this is not done the red shade will be rendered dull by iron compounds.

The water used for dyeing should indicate 2°–3° of hardness (Clarke's scale); if it contains little or no lime, a suitable amount of ground and washed chalk (about ½ per cent. of the weight of the 20 per cent. alizarine paste employed) must be added. Very hard water, or water which contains iron, cannot be used in Turkey-red dyeing.

The dyebath is prepared with 8 to 10 per cent. of alizarine (20 per cent.), 1 per cent. of tannic acid (or 3 to 5 per cent. of good sumach), and about 30 per cent. of ox-blood (of the weight of the cotton). The yarn is entered into the cold dyebath, the temperature gradually raised to boiling during one hour, and maintained so for thirty to sixty minutes longer. After dyeing, rinsing in water is advisable.

The goods now possess a dull red colour, which is transformed by the "clearing" processes into the brilliant Turkey-red shade.

Thirteenth Operation—First Clearing.—The yarn is boiled for four hours in open pans or under a pressure of 3 to 4 lbs. with about 3 per cent. of soda crystals and 3 per cent. of palm-oil soap, dissolved in a sufficient quantity of water.

Fourteenth Operation—Second Clearing.—The yarn is boiled for one to two hours at 3 to 4 lbs. pressure with a solution of 2½ per cent. of palm-oil soap and 0·15 per cent. of tin crystals (of the weight of the cotton), and afterwards thoroughly washed in water. The excess of water is removed by mechanical means (hydraulic press or hydro-extractor), and then the goods are dried in an open-air shed. This closes the long chain of operations.

NEW TURKEY-RED PROCESS.

Sulphated Oil or Turkey-red Oil Process for Yarn and Piece Goods.—This process also yields beautiful red shades, which are, however, not quite as fast as those obtained by the preceding process.

Turkey-red oil prepared from castor oil is most generally used; sulphated oil can be employed, but has not proved so good, as it does not oxidize and polymerize as readily. Very good results are obtained with a carefully made castor oil soap—*i.e.* sodium ricinoleate, but this is not used on the large scale.

First Operation—Boiling.—This is done exactly in the same way as in the preceding processes. Bleaching has to be resorted to in the case of light shades (especially pinks) to obtain bright tints, but the action of the chlorine has to be restricted as far as possible to the destruction of the natural colouring matters of the cotton fibre, while the formation of oxycellulose must be prevented; for this reason, hypochlorite of soda is preferable to bleaching powder or better still is bleaching with potassium permanganate.

Second Operation—Oil preparing.—The washed goods are hydro-extracted, but not dried, and then worked in a bath containing 10 to 20 lbs. of neutralized Turkey-red oil (50 per cent.) for every 10 galls. of water. When thoroughly saturated with the liquor they are evenly wrung out.

Third Operation—Stoving.—The oiled goods are dried at temperatures ranging from 100°–140° F. (40°–60° C.). For the production of a bright and intense red the operations of oiling and drying and subsequent aluming are repeated once or twice. Frequently the oiled goods are steamed under a pressure of 8 lbs. for sixty to ninety minutes, but this is not essential.

The compounds constituting the Turkey-red oil are decomposed by the operations of oiling, drying, and steaming, ammonium or sodium sulphate and various organic acids being formed. The latter are similar to the corresponding substances deposited in the fibre in the older processes, and consist of products of the oxidation and polymerization of ricinoleic acid, etc.

Fourth Operation—Aluming.—The goods are worked for five or six hours in a warm bath 100° F. (40° C.) of red liquor 10° Tw. or of basic aluminium sulphate 10° Tw., well wrung out and dried at 100°–120° F. (40°–50° C.).

Fifth Operation—Chalking.—This resembles the treatments in the other Turkey-red processes by which the material is worked in a weak alkaline bath for the purpose of purifying it from an excess of oil; in this process, however, the purification takes place after the aluming, so that not only is there a removal of oil, but also a more complete precipitation of the alumina which has been absorbed by the fibre during the aluming. A chalk bath is generally employed for this purpose (chalking). Brighter colours are said to be produced when phosphate of soda or ammonium carbonate are employed as fixing agents. Arsenate of soda gives still brighter colours than the phosphate. The cotton is worked for thirty minutes at 90°–100° F. (30°–40° C.) in a bath containing ½ lb. of ground chalk per 10 gals. of water, then thoroughly washed and dyed without drying.

Sixth Operation—Dyeing.—Moderately hard water free from iron, exactly as in the emulsion process, is required For very deep shades about 15 per cent. of alizarin (yellow shade) is necessary; a fine pink is obtained by this process with 1 or 2 per cent. of alizarin V. The whole quantity of the dyestuff is added to the dyebath, and the goods are introduced at a temperature not exceeding 25° C. and turned for twenty minutes; in about half an hour the bath is heated to 140°–160° F. (60°–70° C.), and maintained at this temperature for one hour. After dyeing, the goods are wrung and dried with or without previous washing.

Seventh Operation—Second Oil preparing.—The material is impregnated once more with a solution of neutralized Turkey-red oil (5 to 10 lbs. per 10 galls.) and dried. The second oiling may be dispensed with or take place after the mordanting. In the latter case a fresh treatment in a weak solution of basic aluminium sulphate or red liquor follows for the purpose of fixing the oil.

Eighth Operation—Steaming.—The goods are steamed for one hour at 15 lbs. pressure or two hours without pressure to develop the colour. According to a more recent process, neither oiling nor steaming follows the dyeing; the dyed goods are simply heated for some hours in water under considerable pressure. It is said that the beauty increases up to a pressure of about 65 lbs. When the goods come from the dyebath they possess an orange tinge, and a part of the dyestuff can be stripped by rinsing in water, since it is not intimately combined with the mordants. The complex lake is formed by steaming only, and the material then receives a dull red colour which is brightened by the clearing baths.

Ninth and Tenth Operations—First and Second Clearings.—These operations may be executed as in the older processes; but less severe treatments are sufficient. A fine brilliant red is produced by once or twice boiling under 4 to 8 lbs. pressure for thirty to sixty minutes in ½ per cent. soap solutions (without any further additions). The soaped goods are well washed in water and dried at a moderate temperature.

The process can be simplified by raising the temperature of the dyebath to the boiling point. In this case the oiling after dyeing is to be omitted, and the steaming may be dispensed with. But the shade is never so bright or fast as that of the colours which have been produced at a lower temperature with subsequent steaming.

Silk.—The true alizarine dyestuffs yield on silk shades of excellent fastness to light, boiling soap and washing. They are largely used for what is termed fast work or boiling shades, chromium being the mordant employed. In order to preserve the lustre of silk, it is not mordanted in the same way as wool, but in the following way :—Mordant the silk overnight in a cold bath of chromium chloride 32° Tw., or chrome alum 9° Tw., then wring out, wash thoroughly, work half an hour in a cold bath of sodium silicate ¾° Tw., and wash thoroughly. By this means basic chromium salts are precipitated on the fibre. Dyeing is carried out in a boiled-off-liquor bath broken with acetic acid: enter the silk cold, give a few turns, raise the bath to the boil in ¾ hour and dye at the gentle boil one hour; wash off and brighten in weakly acidulated water.

The fastness of the shades obtained by this method varies with mordant dyestuffs other than the true alizarine series. Preliminary tests should always be made of such a dyestuff before it is dyed on the large scale.

In cases such as the dyeing of silk noils in which the preservation of the lustre is not of great importance, the topchroming and metachrome methods may be used with advantage; for details see under wool.

Wool.—The mordant dyestuffs are of the highest importance, and are largely used in the dyeing of all classes of woollen and worsted goods, for which the greatest possible fastness is required, *e.g.* Scotch tweeds, West of England cloths, fine worsteds, etc. They are applied in practice by the three following methods :—

1. Chrome mordant.
2. Topchroming mordant.
3. Addition of bichrome at the start (metachrome method).

Each of the three methods have their advantages and disadvantages according to the class of work being done.

The chrome mordant method is the oldest method, and the application of the true alizarine dyestuffs is confined to this method, but other mordant dyestuffs, such as diamond black, are more frequently applied by Methods 2 and 3. It may with fairness be stated that Methods 2 and 3 are destined to oust Method 1 for most work. I have not, however, the least hesitation in stating that the chrome mordant method is easily the best for fancy shades on yarns and pieces, both for level results and ease of matching off. For bulk work in blacks and blues Method 2 is widely adopted, whether in the form of loose wool, slubbing, yarn or pieces, but for general work in loose wool and slubbing Method 3 has special advantages.

Chrome Mordant.—This mordant is practically the only mordant used nowadays, whereas when the old dyewoods were in vogue iron, tin, alum, and copper were largely used as well as chromium. The disadvantage of this process is that it is a two-bath process, which involves more labour, steam, time, and water, all of which are factors which modern tendencies in dyeing are always striving to reduce. Nevertheless, it has solid advantages for certain classes of work which induces its use.

In piece dyeing chrome mordanting always has the effect of cleaning the pieces and thus favouring level results. From the dyer's point of view it is the safest method for dyeing fancy shades on pieces and yarns, because correction of shade is easiest by this method. For certain classes of loose wool dyers still favour the chrome mordant, though the improvement both of the other methods and the suitable dyestuffs is reducing this advantage.

There are several methods of fixing the chrome on the fibre, potassium or sodium bichromate being used as the source of the chrome, whilst various assistants are used. It is surprising what different results may be obtained from one and the same colour by using different assistants.

Hematine crystals are marketed in different states of oxidation, and consequently give different results according to the mordant employed. If wool is mordanted with 3 per cent. bichrome and 1 per cent. D.O.V. chromic acid is fixed on the fibre and yields what is termed an oxidizing mordant, whereas if the wool is mordanted with 3 per cent. bichrome, 2½ per cent. cream of tartar, chromic hydroxide is fixed on the fibre and yields a reduced mordant. It follows, therefore, that a well-oxidized hematine crystals will give a better result on a reduced than an oxidizing mordant, conversely a partially oxidized hematine crystals will give a better result on an oxidizing than on a reduced mordant. Brilliant alizarine blue R gives the best result on a weak bichrome and oxalic acid mordant.

Gallocyanine gives shades fastest to rubbing on a bichrome and cream of tartar mordant, whilst with bichrome and D.O.V. formic or oxalic acid the shade rubs badly. Alizadine brown M also illustrates the influence of the assistant used. When dyeing heavy shades with this colour on a chrome mordant, it must be dyed on a bichrome and acid mordant, and not on a bichrome and cream of tartar mordant, in order to get shades perfectly fast to milling.

In practice, however, my experience is that bichrome alone is the mordant most commonly used, because price is often a governing factor to the extent of preventing the dyer giving a better dye.

The following are the various mordants used and their method of application.

Bichrome alone.—Boil 1–1½ hours with 2–4 per cent. bichrome; many dyers keep a standing bath and replenish with three-fourths of the original amount taken. Sometimes sulphuric acid (one-third of the weight of bichrome) is added; this is most frequently used for logwood.

Bichrome and tartar.—Boil 1–1½ hours with 1–3 per cent. bichrome, and ¾–2½ per cent. tartar. This is more expensive than the former, but is largely used, especially for the best class of trade.

Bichrome and Oxalic Acid.—Boil 1–1½ hours with 1–3 per cent. bichrome and 1–3 per cent. oxalic acid.

Bichrome and Formic Acid.—1–2 per cent. bichrome and 1–2 per cent. formic acid (85 per cent.). Since the reduction of the bichrome with this assistant takes place rapidly, uneven dyeings result, unless the mordanting is carefully carried out. The wool should, therefore, be entered at 140° F. (60° C.), and the wool worked whilst the bath is gradually brought to the boil, then boiling continued 1–1½ hours. The bath will be exhausted clear of chrome.

Bichrome and Lactic Acid.—1½–3 per cent. bichrome, 3–5 per cent. lactic acid (50 per cent.), 1 per cent. D.O.V. The remarks under *Bichrome and Formic Acid* apply here also.

Bichrome and D.O.V.—Boil 1–1½ hours with 3 per cent. bichrome and 1 per cent. D.O.V. This mordant is frequently used for logwood and hematine. Wool when mordanted with bichrome alone or bichrome and D.O.V. has a yellow colour due to the presence of chromic acid, whilst with the other mordants the wool has a green colour due to the presence of chromic hydroxide on the fibre, which has been formed by the reduction of the bichrome.

Results in practice have shown that an old mordanting bath when using bichrome alone gives better results than a fresh bath, so that dyers work the mordanting bath continuously.

When bichrome and formic acid are used it will be noticed that much less bichrome is used, the whole being precipitated on the fibre. The bath is so well exhausted of chrome that the same liquor may be used for dyeing as was used for mordanting.

All mordanted wool must be thoroughly washed before dyeing or else the dyed shade is very liable to rub badly.

Iron Mordant.—Mordant in the same way as above, only using 3 per cent. copperas and 2½ per cent. tartar.

Alum Mordant.—Mordant in the same way as above, only using 8–10 per cent. alum and 3–5 per cent. tartar.

Dyeing.—Fill the cistern with cold water, add 1–2 lbs. acetic acid according to the hardness of the water. The pastes are mixed with acidulated water to a thin uniform paste, which is run into the dyebath through a fine sieve to prevent lumps getting into the bath, which might cause uneven dyeing. Powders are dissolved in boiling water before adding to the bath. After raking the bath well, enter the wool cold, and work at a low temperature till most of the colour is absorbed, especially when dyeing alizarines in the form of bisulphite compounds. When using bisulphite compounds the bath must not be raised above 150° F. (65° C.), until all the colour has been absorbed, because above this temperature the bisulphite compound splits up, and unless it has been absorbed by the fibre it precipitates insoluble alizarine dyestuff in the dyeliquor, which wastes dyestuff and causes the colour to rub. The bath is gradually raised to the boil, and dyeing is continued at the boil for 1-2 hours. If a very heavy shade is being dyed it is advisable to add ½ per cent. bichrome to the dyebath when exhausted, and boil ¼ hour longer. This prevents any bleeding in the subsequent milling.

Topchroming.—This is a modification of what dyers of the old school used to call the "saddening" process in the dyeing of the old dyewoods. This process is universally used for blacks, also largely for blues, but its adoption for fancies has proved slower because of the difficulty in matching off. This difficulty arises owing to the fact that the shade cannot be judged until the colour has been developed with the bichrome; now the difference in shade before and after the addition of the bichrome is often very marked, so that a good deal of experience is required to match accurately. However, the difficulty of shading in a hot chrome liquor is not so great now that there are colours at the dyers' disposal quite suitable for this purpose.

If the amount of shading required is only slight, then acid colours should be used, but should the shade require a large addition of colour, say ½ per cent. or more, then the above chrome colours should be used. When shading, shut off the steam and add the well-dissolved colour, put on steam again and boil ¼ hour. In the case of loose wool, throw on the well-diluted colour solution as uniformly as possible and have the wool well poled.

The great advantage of this process is that it is a short one, and therefore economical in time, labour and steam;

whereas the material is consequently left in better condition. In the case of loose wool it is loftier and spins better. The results obtained are excellent as regards fastness, indeed better than some of the same colours applied on a chrome mordant. The method is being largely used and competition is forcing the most reluctant dyers to adopt it. It is most suitable for loose wool (especially for big lots of one shade, such as khaki), since if one batch comes off shade, another lot may be dyed accordingly to counterbalance it to carry it through the blending. For yarns and pieces, one has not the same latitude that one has in loose wool, so that its use is confined mainly to blacks and blues.

The dyeing is carried out as follows:—The colour is boiled along with the Glauber's salt in about a foot of water at the bottom of the cistern; when the colour has dissolved the bath is run up with cold water, 1–5 per cent. acetic acid is added, and the bath well stirred. The material is entered, the bath is gradually raised to the boil in ½ hour, and dyeing continued at the boil for ½ hour. If the bath is not exhausted, ½–1 per cent. sulphuric acid is added and boiling continued ¼–½ hour longer to exhaust the bath. When the bath is exhausted and not before, ½–2 per cent. bichrome is added, and boiling continued ½ hour. It has proved advisable in practice when dyeing wool which has subsequently to be heavily milled with mercerized cotton to continue the boiling in the chrome up to ¾–1 hour. The effect of the additional boiling is very beneficial in preventing bleeding on the cotton. No delay should take place before the wool is washed off, to avoid the shade changing, due to the prolonged action of the hot acid chrome liquor; also from the point of view of the spinning qualities of the wool.

Piece Goods.—The following process should be adopted for the best classes of pieces, to ensure perfect penetration, but when time is an object, and the goods of a low quality, the process can be considerably shortened. A cold dye-bath is stuffed with the requisite amount of colour, and 10 per cent. Glauber's salt, raise the bath to the boil in 1 hour, add 2½ per cent. acetic acid, boil ½ hour, add a further 2½ per cent. acetic acid, and boil ½ hour, when the bath should be exhausted; if not, add ½–1 per cent. D.O.V. and boil a little longer. When the bath is exhausted, add 1–2 per cent. bichrome, according to the depth of shade, and boil ½ hour longer. When dyeing pieces containing white cotton effects, add 2–3 per cent. D.O.V. instead of ½–1 per cent. and boil a full ½ hour before adding the bichrome.

Fast Chrome Blacks.—This class of blacks, of which diamond black was the first representative, are of enormous consumption in the dyeing of all forms of wool, so that they have received a large amount of attention at the hands of the colour manufacturer. The first members of this class of dyestuff were not fast to potting. Potting is a process mainly carried on in the West of England for giving a special finish to the cloth. It consists in wrapping the cloth round a roller and immersing it in water for twenty-four hours at various temperatures. The cloth is then raised on the gig and may be subjected to as many as six immersions and raisings before the requisite finish is obtained. It is essential that the dyestuff used does not bleed into adjacent white or coloured threads. The only blacks which would withstand this process were logwood black and alizarine black. The earlier chrome blacks, like diamond black F., would not. Of recent years there has been a large range of what are termed potting blacks introduced, of which the first was diamond black P.V. They usually have the prefix P. attached to them, as an indication that they are fast to potting, but their merits in this respect vary considerably They are quite distinct from the non-potting variety in that they are more soluble, will stand much more sulphuric acid in the dyeing, and require more bichrome to fully develop the shade. These very properties have made them an ideal black for the dyeing of carbonized rags. If carbonized rags are dyed with the diamond black F. class the acid in the rags so quickly exhausts the colour that it is only dyed on the surface of the rags, with the result that when they are subsequently pulled up they appear grey, due to lack of penetration. Now, the P.V. class, owing to their greater solubility and less sensitiveness to acids, do not dye on so quickly, and therefore give better penetration. For this reason they have become of the highest importance in the rag-dyeing trade. As a rule the potting blacks are not of the same fastness to light as the non-potting blacks. Diamond black P.V. is not as fast as diamond black F., but, like every rule, it has its exceptions in eriochrome black T. and T.G., which possess excellent fastness to light. Whilst both classes of blacks possess excellent fastness to milling, the P. brands are the faster in that they leave mercerized cotton effects cleaner in the heaviest milling—mercerized cotton being most difficult to keep untinted in milling.

Fast chrome blacks, when dyed as detailed below, possess remarkable fastness to milling, light, acids and alkalies; they may be dyed without detriment in copper vessels, and are quite suitable for machine dyeing. The method of dyeing is as follows:—

Charge the dyebath with the requisite amount of colour, 10 per cent. Glauber's salt, and 5 per cent. acetic acid; enter lukewarm, raise to boil, and dye boiling ½ hour, then add ½ per cent. sulphuric acid; boil 20–30 minutes, when the bath should be exhausted, then add 1 per cent. bichrome and boil ½ hour. In no case must the bichrome be added until the bath is exhausted or else a brown shade black will be the result. If ½ per cent. sulphuric acid does not exhaust the bath then more sulphuric acid must be added, until the bath is exhausted; however, ½ per cent. sulphuric acid wil be found sufficient under ordinary circumstances to exhaust the bath up to 8 per cent. colour. Within certain limits the shade of the fast chrome blacks may be controlled by the amount of sulphuric acid and bichrome which is used thus ½ per cent. sulphuric acid and 1 per cent. bichrome will give a much bluer shade than 2 per cent. sulphuric acid and 2 per cent. bichrome, which will yield a dead black.

If the black has to be subsequently heavily milled with mercerized cotton, it is advisable to boil ¾–1 hour in the bichrome, because this has a beneficial effect in preventing bleeding. The two places in which it is possible to go wrong when dyeing chrome blacks are as follows :—The sulphuric acid must not be added till the bath has boiled at least ½ hour, or else the colour will be dyed on too quickly, so that proper penetration will not be obtained, probably coupled with uneven results ; the bichrome must not be added till the dyebath is exhausted or else results which rub will be obtained, coupled with a poor shade of black tending to brown.

Potting chrome blacks are dyed as above, except that 2–3 per cent. sulphuric acid must be added to exhaust the bath instead of ½–1 per cent., and 2–3 per cent. bichrome must be added in order to fully develop the black.

The chrome blacks before chroming are dull claret shades, which are converted to black on boiling with the bichrome. The chrome blacks do not give satisfactory shades on chrome mordant and are practically never applied by this method. They may be dyed by the metachrome method, but the results are not as satisfactory as when they are topchromed.

True alizarine dyestuffs are never applied by this method, with the possible exception of alizarine red S. powder, which is a sulphonated and therefore soluble alizarine.

Chromotrope Dyestuffs.—These are easy levelling red acid dyestuffs, which are indeed used as acid reds of very good fastness to light, but which on chroming are turned into blue shades of great fastness to light and washing. They are largely used for the dyeing of navy blues on pieces, and have become standardized for certain classes of dress goods. Many of the dyestuffs so used are combinations of chromotrope acid (Di oxy naphthalene di sulphonic acid 1 : 8 : 3 : 6) with various bases, hence the name.

They are dyed like ordinary acid dyestuffs with Glauber's salt and sulphuric acid, but after ½–1 hour's boiling 1–3 per cent. bichrome, 1–3 per cent. lactic acid and 1 per cent. D.O.V. are added, and boiling is continued ½–1 hour. The shade gradually changes from red to navy blue as the boiling proceeds, so that a large range of blues may be obtained, according to the length of time of boiling in the bichrome. The longer the wool is boiled with the bichrome the greener does the shade develop: the addition of more bichrome has exactly the same effect. Since many of the navy blues so obtained are on the red side, it is common practice to add a little acid green to neutralize this redness. The lactic acid may be replaced by formic acid or may be omitted altogether. Too much acid tends to delay the full development of the shade; copper salts act similarly.

Addition of Bichrome at the Start.—This modification of the topchroming process was originated by the Berlin Aniline Co. by a patent in 1900, dealing with a special mordant called metachrome mordant. This mordant consisted of a mixture of potassium chromate and ammonium sulphate. The chemistry of the mordant is as follows:—When the dyeliquor is boiled ammonia is gradually evolved and sulphuric acid formed in the dyebath, which at once converts the chromate present into bichromate, which acts on the colour and fixes it on the fibre as the chrome lake. This mordant was added to the dyebath along with the colour, and no precipitation took place, so that it was possible to dye in one bath with the mordant at the start. Now, if bichrome is added to the dyebath along with certain dyestuffs immediate precipitation of the dyestuff, as the chrome lake, takes place. If, however, the bichrome is first made alkaline with ammonia, *i.e.* converted into chromate, no precipitation takes place. There is a large range of dyestuffs suitable for use with this mordant now obtainable, but many dyestuffs—true alizarines, also gallocyanines—are precipitated even by the chromate and so may not be used.

Nowadays the dyer usually makes his own metachrome mordant, in that he uses bichrome and makes it alkaline with ammonia, thus converting it into chromate, whilst if he uses ammonium sulphate—also made alkaline—as assistant he imitates the mordant exactly. Acetic acid, formic acid, sulphuric acid or nitre cake may also be used as detailed hereafter.

There are two pitfalls in this process which must be avoided:—

1. The dyestuff and bichrome must be dissolved

separately, and on no account may they be boiled together, or precipitation will take place.

2. The bath at the outset must be slightly alkaline with ammonia : to this end the bichrome must be made alkaline, also the ammonium sulphate, if used, must be made alkaline, because it reacts acid ; if acid is used it must not be added till the bath has boiled at least half an hour ; if formic acid, sulphuric acid or nitre cake is used it must be added extremely slowly.

The following instructive experiments will illustrate the necessity of this. To a hot solution of alizadine brown M. add a little bichromate solution, when precipitation of the colour will immediately take place : now repeat the experiment, but before adding the bichromate solution neutralize it with ammonia, when no precipitation will take place : next add acid to this solution until it is acid, when precipitation immediately takes place.

This process, which is alternatively known as monochrome, chromate, and autochrome, has one distinct advantage over the other two methods already described. As compared with chrome mordant it is a single as against a two-bath process, which is a great economy in time, labour, and steam, coupled with increased output. Compared with the topchroming method, the development of the shade is more gradual, so that the dyer is sooner able to see how the shade is developing. It has, therefore, achieved great popularity in loose wool, slubbing, and yarn dyeing, but has not been adopted for piece dyeing due to the difficulty in adding colour to the dyebath for shading purposes towards the end of the dyeing operation.

The method of dyeing is as follows :—

Boil the colour in the bottom of the cistern for ten minutes in order to completely dissolve it, then fill up the bath, add the requisite amount of bichrome and ammonium sulphate separately dissolved from the dyestuff and made alkaline with ammonia. In the case of loose wool or slubbing enter into the boiling dyebath, but in the case of yarn it is advisable to enter not higher than 140° F. (60° C.). Dye

1 hour at the boil, when the shade should be fully developed. In my opinion ammonium sulphate gives the best result, but it may be replaced by acetic acid. If acetic acid is used it must not be added till the bath has boiled half an hour, and then it must be strongly diluted. Some dyers use formic and sulphuric acid, but I deprecate their use, because unless they are added very skilfully they do more harm than good. The average amount of bichrome required is half the total weight of the colour used, but the proper amount is always given by the respective colour makers. For every pound of bichrome used add 2½ lbs. ammonium sulphate, 2½ lbs. acetic acid, 4 lbs. nitre cake or 1 lb. formic acid. The minimum quantity of bichrome which should be used is [illegible] per cent. of the wool, because it must always be remembered that the wool itself absorbs a certain quantity. Other colours than mordant dyestuffs may be used by this process, so long as the colour withstands the action of the bichrome, and it is fast to milling and light: coomassie navy blue, indocyanine B and patent blue have been largely used by this process because suitable blues of the mordant class were not numerous.

The results obtained by this process possess excellent fastness fully equalling the results obtained by the other processes in most cases. Navy blues and blacks are, however, not dyed by this process for lack of really suitable dyestuffs.

When dyeing skin wool, *i.e.* wool which has been removed from the pelt by lime, and therefore full of lime, it must be noted that the colour takes longer to develop since the development is retarded by the alkalinity of the lime. More acid may, therefore, be needed. This process is particularly suitable for machine dyeing and requires no special precautions, except that it is advisable not to add the bichrome-made alkaline with ammonia until the dye-liquor has been circulated a quarter of an hour at the boil. This precaution ensures the material being thoroughly saturated with the dyestuff before the bichrome commences fixing it on the fibre.

For shading purposes acid colours fast to milling may be used, such as patent blue or else mordant dyestuffs, which are not precipitated by bichrome and acid. In the case of yarn it is best to neutralize the bath with ammonia before adding the dyestuff, but with loose wool this will not often be necessary. Steam is. of course, shut off whilst the perfectly dissolved dyestuff is added.

GENERAL NOTES.

Owing to the mordant dyestuffs being so fast it naturally follows that they are very difficult to remove from the fibre. Uneven shades are, therefore, very difficult to correct. One of the best methods of achieving this is to boil the wool with fairly strong sulphuric, hydrochloric or oxalic acids, which has the effect of splitting up the chrome-dyestuff lake. Follow this bath with a warm ammonia bath, which will often remove the dyestuff which has been split off the chrome by the acid treatment.

One weakness of the alizarine dyestuffs is their liability to rub. This cannot altogether be stopped, but scrupulous care both in mordanting and dyeing, coupled with correct choice of mordant, can reduce it to a minimum.

Lime wool is a source of trouble to dyers by whichever method it is dyed: dyers usually favour the chrome mordant method. Sulphuric acid must be avoided, or else one obtains the insoluble calcium sulphate precipitated on the wool. When chrome mordanting a good plan is to mordant with bichrome and sufficient hydrochloric acid to remove all the lime in the very soluble form of calcium chloride.

SECTION V.—DIRECT COTTON DYESTUFFS

THE first member of this class of dyestuffs to appear on the market was Congo red, which was discovered in 1884 by Böttiger. Though the fastness of this colour left much to be desired—particularly its fastness to acids—it met with a ready sale until it was supplanted by benzopurpurine 4B. It may incidentally be remarked that Congo red has experienced quite a revival during the war owing to the impossibility of making benzopurpurine 4B due to the demand for toluol for explosives.

The fact that Congo red was able to be dyed on cotton and other vegetable fibres without any previous mordanting —hitherto indispensable—made its discovery epoch-making in its influence on the dyeing trade. Its importance was immediately grasped by the coal tar colour manufacturers, who displayed intense activity in discovering new bases and new acids from which new dyestuffs could be made. The result of this activity is shown in the large range of excellent direct cotton dyestuffs which are known to the dyeing trade to-day. The simple method of application was welcomed by the dyers, with the result that the recent United States Dyestuff Census revealed the fact that they possess the largest consumption of any class of coal tar dyestuffs.

Like most groups of dyes individual members possess the most divergent properties. It includes Congo red, which is so sensitive to acids that it is largely used as an acid indicator, but it also includes benzo fast scarlet 4B.S, which is so fast to acids that it will withstand treatment with strong nitric acid. It includes a colour as fugitive to light as primuline, and one so exceptionally fast to light as chlorazol fast yellow B.

It may, however, be claimed that the progress in this class of dyestuff has been continuous in the introduction of colours of improved fastness, so that the class now includes a large range of dyestuffs of excellent fastness. It must not be thought, however, that there is no scope for further improvement—on the contrary, there is great scope, as the following example will show. In chrysophenine we have a dyestuff of rich shade coupled with good fastness to light, but it is very poor to washing, in that it readily stains white cotton washed with it. In chlorazol fast yellow B we have a dyestuff of very good fastness to washing and light, but of a poor shade compared with chrysophenine. The dyeing trade requires a direct cotton yellow of the rich shade of chrysophenine coupled with the fastness to washing of chlorazol fast yellow B.

Methods of after-treatment—which are fully detailed hereafter—have been discovered which considerably improve various properties of certain individual colours.

The enormous extension in the dyeing of mixed fabrics of silk, wool, cotton and artificial silk must be credited to the direct cotton dyestuffs, whilst the increasing success of present-day garment dyeing is directly attributable to the same colours.

The direct cotton dyestuffs—following the classification adopted by Green—include five groups of colours from the chemical point of view, though from the dyeing point of view they are one class. The five groups include—

Disazo colours.	Benzopurpurine 4B.
Trisazo colours.	Titan black FF.
Tetrakisazo colours.	Toluylene brown R.
Stilbene colours.	Mikado orange.
Thiazol colours.	Primuline.

At the present time it is impossible to offer any definite opinion on the theory of the dyeing of the direct cotton dyestuffs. The consensus of opinion of those who have investigated the subject is that the process is purely mechanical. Witt advanced the theory that a solution of the dyestuff in the cotton fibre takes place, and that the effect of salt addition to the dyebath decreases the solubility of the dyestuff in water, and so favours the solution in the fibre. The fact that repeated boiling with plain water enables one to strip the colour from the cotton points to the dyeing being merely mechanical, but it should be pointed out that with many of the fastest direct cotton dyestuffs it is impossible to remove any appreciable quantity by boiling with water. According to Minajeff, fibres dyed with direct cotton colours show, when microscopically examined, a weak homogeneous colouring of fibre membrane coupled with stronger colouring of periphery of fibre. Dr. Haller has published some interesting work (Lehne's *Farber Zeitung*, 1914, p. 306) in support of the colloid or physical theory of dyeing, using primuline as the colour; but the work will have to be extended to other typical colours before it can be seriously considered. As regards a chemical theory of dyeing for cotton it should not be lightly dismissed because, as is cogently pointed out in "A Manual of Dyeing" (p. 19), cellulose is by no means as chemically inert a body as is sometimes thought.

APPLICATION.

Dissolving.—The direct cotton dyestuffs are for the most part freely soluble, nevertheless the best course to pursue is to stir the colour into a smooth paste with cold water and then pour on boiling water—condensed water for preference—whilst stirring. This precaution prevents the colour from floating on the surface, as is possible if the boiling water is poured straight on to the dry colour or if the dry colour is added to the dyebath. This precaution should be adopted with all classes of colour, because it is one factor in obtaining perfectly level results. I am aware it is frequently not carried out in practice, but nevertheless the above method is the surest and safest way to avoid bad results due to fleckiness.

For the convenience of the dyehouse routine many of the standard colours which are in constant use are kept in stock solutions ready for use. The additions of colour to the dyebath for shading purposes are usually very small, so that standard solutions of the colour used enable the dyer to measure out the requisite amount of colour to be added accurately and quickly.

Cotton.—The average direct cotton colour does not exhaust very well, so that a fair amount of dyestuff is left in the dyebath. It follows, therefore, that the volume of liquor used plays an important part in the depth of shade obtained. On the grounds of economy the volume of liquid should be kept as low as possible, but this should not be carried out too far, because the cost of dyestuff so saved is nothing compared with the cost of correcting a batch of goods spoilt through not having sufficient liquor in which to work them efficiently. In open cistern dyeing 30 times liquor calculated on the weight of cotton is the minimum quantity in which loose cotton may be efficiently dyed if the cotton has to be poled (stirred) by hand: for yarn 20–25 times liquor calculated on the weight of cotton is the average amount used in the ordinary yarn beck: for piece dyeing jiggers are used in which the amount of liquor taken will not be more than six times the weight of the cotton. Moreover, the increasing adoption of dyeing machines for loose cotton, yarn, cops, cheeses, and beams reduces the amount of liquor used to as low as five times the weight of the cotton.

Assistants used.—Owing to the direct cotton dyestuffs not exhausting an assistant is added to the dyebath to decrease the solubility of the dyestuff, and thus increase its affinity for the fibre. The three assistants used for this purpose are Glauber's salt, sulphate of soda, and common salt. Each of them have their respective merits, in connection with which it must be remembered that 5 parts common salt =6 parts sodium sulphate (desiccated Glauber's salt) =12 parts Glauber's salt. It may be generally stated that Glauber's salt is used for the dyeing of pale shades, whilst common salt is used for medium and heavy shades. In countries like Italy where common salt is subject to a revenue tax its cost prohibits its use in dyeing; where difficulty is experienced in getting level results—say in compound shades—Glauber's salt should always be given the preference over common salt.

The average amounts required are indicated below :—

0·1 per cent. colour.	10 per cent. Glauber's salt.
½ per cent. colour.	15 per cent. Glauber's salt.
1 per cent. colour.	10 per cent. common salt.
2 per cent. colour.	20 per cent. common salt.
3 per cent. colour.	30 per cent. common salt.
4 per cent. upwards colour.	40 per cent. common salt.

Soda ash and other alkalies have the effect of increasing the solubility of direct cotton dyestuffs, therefore their use in the dyebath decreases the rate of absorption by the fibre. Their use is, therefore, to be recommended with colours which have a low solubility, such as diamine brown M. Its use is also advantageous in cases of cloth and tightly twisted yarns, which are difficult to penetrate, since soda ash increases the solubility and therefore the penetrative powers of direct cotton dyestuffs. If the material is boiled for some time with the dyestuff and soda ash alone, then the common salt or Glauber's salt subsequently added, these conditions are the most favourable for obtaining complete penetration of material which is difficult in this respect.

If the water used for dyeing is hard, the use of Glauber's salt or sulphate of soda should be avoided so as not to form sulphate of lime, which will make the finished cotton hard in cases where a soft finish is desired.

The use of soda ash has, however, one disadvantage, which should always be borne in mind. Shades dyed with direct cotton dyestuffs, if allowed to lie wet for some time, are liable to run, *i.e.* the portion of the material to which the water drains is liable to be darker than the rest; this defect is much more pronounced if soda ash is used in the dyeing, due to the colour being more soluble when it is used. For example, if dyed yarn is allowed to hang on sticks in the wet state for any length of time before drying, the lower part of the yarn is liable to be darker than the upper part, due to some of the colour draining along with the water to the lower part—particularly if the cotton has not been well washed—a point in which carelessness is often shown.

Phosphate of soda is sometimes used in cotton dyeing in order to brighten the shade, such as pale shades of yellow.

Soap and soluble oil are frequently used in cotton dyeing, particularly for delicate shades on mercerized cotton and artificial silk in order to yield the brightest shade possible coupled with a slow rate of dyeing so as to give level shades. Their effect is on the same lines as soda ash, in that they retard the rate of dyeing. It must, however, be remembered from the very nature of their effect in the dyeing that the dyebath is by no means so well exhausted as when they are omitted.

Acetic acid has a very limited use in cotton dyeing, chiefly in dyeing bright blues of the Titan Como class.

Dyeing.—In principle the dyeing of cotton with direct cotton dyestuffs is simplicity itself, in that dyeing is carried out at the boil for ½-1 hour. In actual practice, whilst it is a short process, there are several factors which have to be taken into consideration and which demand the experience and judgment which are the qualification of the foreman dyer. Some of these are indicated below. The temperature at which direct cotton dyestuffs dye varies considerably with the individual dyestuffs: *e.g.* chrysophenine G will dye cotton almost as full a shade at 100° F. (40° C.) as it does at the boil: on the other hand, benzo fast scarlet 4BS does not appreciably go on to cotton below 140° F. (60° C.). It follows from this that different colours dye at different rates. This may be the cause of considerable trouble in the dyeing of compound shades, because the use of colours dyeing at different rates has a tendency to give flecky results, in which the individual colours may be picked out on the fibre.

For the purpose of dyeing compound shades very soluble colours—such as B.H. blacks—should be chosen which do not dye on too quickly, particularly must such colours be chosen for shading purposes. This is best illustrated by an example: diamine brown M is not a soluble colour, chlorazol deep brown B is a very soluble colour. It would be courting disaster to add a small quantity of diamine brown M to a boiling dyebath, because it would dye on too quickly and therefore unevenly, due to its comparative insolubility. On the other hand, chlorazol deep brown B could be used with safety under the same circumstances, due to its ready solubility and to the fact that it does not rush on to the fibre.

Again, some dyestuffs will not mix with other dyestuffs despite every precaution being taken to ensure the best results. Direct cotton yellows of the Curcumine S class will not dye level with chlorazol blue B in compound shades, but will dye level with chlorazol black E.

If a shade comes out heavier than the desired shade or uneven, it may be sufficiently stripped in many cases by boiling in a clean bath with soda ash and Glauber's salt. If this treatment is not sufficiently effective, the colour may be stripped with hydrosulphite or by a mild treatment with bleaching powder. In very few cases are the dyebaths exhausted in the case of direct cotton colours. On the face of it it is therefore economical to keep up the dyebaths, but in practice it is not always feasible. With the exception of shades for which the dyer may have a constant demand, such as blacks, navies, and reds, it is not possible to maintain the baths due to lack of cisterns. Moreover, in the case of pale and medium shades the amount of colour left in the bath is negligible when calculated at normal prices. Where machines are used it is easier to reserve several liquors by having several storage tanks.

Old dyebaths should be replenished with three quarters of the original amount of colour taken and one quarter of the original amount of assistants.

Care should be taken to avoid too much common salt in the dyebath, which would precipitate the dyestuff. The cold dye liquor should not stand at more than 6–8° Tw. when dyeing dark shades.

Dyeing of Cotton Hank with Direct Cotton Colours.—Before dyeing the yarn should be well boiled out and bleached if it is intended to use it for light shades. Cotton yarn is generally boiled in one of the many forms of low-pressure kiers. The yarn is packed into the kier and boiled with the addition of 3–5 per cent. soda ash overnight. If a kier is not available the yarn should be sewn up in canvas bags and boiled in a bark for at least 8 hours.

When dyeing in barks it is preferable that the liquor should be heated by a coil to prevent dilution of the liquor by condensation of steam. As heating a bark by a steam coil takes rather a long time, a direct steam pipe should also be fitted to the bark, so that the bath may be brought to a boil by means of direct steam, and kept at a boil by means of the coil. In dyeing the yarn is usually entered at 140° F. (60° C.), given a couple of turns, the bath then brought to the boil and dyeing continued at the boil for ½–¾ of an hour. When dyeing dark shades the yarn may be entered direct into the boiling bath, and after three-quarters of an hour's boiling, shut off steam and allow the yarn to feed in the cooling bath. If difficulty is experienced in getting any shade even, start the bath with soda ash, but without salt or Glauber's salt, and only add it after the yarn has been boiled a quarter of an hour.

Direct Cotton Colours on Loose Cotton.—Dyeing loose cotton with direct cotton colours is very simple. The dyeing is usually carried out in large wooden vats or in pans made of brick and lined with iron heated by steam; some of the latter are also heated by direct fire. The boiling bath is charged with the colour and the dry cotton thrown in; when it has been boiled under, the cotton is poled a quarter of an hour, the salt thrown on and poling continued another quarter of an hour. The bath is kept at the gentle boil for ½–1 hour, then the bath is let off in case of pale shades. Heavy shades are preferably allowed to steep 2–3 hours or left overnight.

Cotton Warps dyed with Direct Cotton Colours.—The direct cotton colours are very largely used in dyeing shades on warps to be woven into flannelettes, zephyrs, shirtings, etc., also for producing very cheap imitation indigo shades. The warps are boiled out in a four-box machine, if necessary, but it is usual in well-managed dyehouses to get the majority of shades by passing the warps through a boiling solution of the colour, feeding up and keeping the warps straight as they pass through the machine, and thereby boiling and dyeing them at one end.

Sky blues, pinks, creams, yellows, etc., may all be dyed at one end, provided that the labourer in charge of the machine is reasonably careful. The warps should be doubled up so as to make the run as short as possible and thereby avoid getting the warps ended by incorrect feeding up. If an end is run before the warps are sent through the machine, it is a very simple matter to dye nearly every shade produced by the direct cotton colours at one end.

Many shades are now dyed on cotton warps by adding the colour solution to the size. A good red may be obtained with two ends through the sizing machine, while creams, lavenders, fawns, pinks, etc., may be finished at one end, though it is not so easy to keep the warps from running off as when dyeing in the ordinary machine. Direct shades on warps are matched as nearly as possible in the dyehouse, and then topped in the sizing machine with basic colours to the exact shade required.

The Direct Cotton Colours on Cotton Pieces.—Before the actual dyeing takes place, cotton piece goods are usually prepared in some manner. The first process in the preparation of sateens and similar materials is singeing. The object of the singeing process is to get rid of loose fibres from the face of the cloth. Care should be taken to keep the singe-rollers or plates free from scale, and this is usually removed by means of a long-handled file. After singeing the pieces are crabbed and steamed on perforated cylinders. For pale and bright shades the pieces are bleached after boiling. Heavy goods such as moleskins, corduroys, velveteens, etc., are usually prepared for dyeing by boiling with or without pressure in a dilute solution of soda ash.

This process removes size and other impurities which might effect the appearance of the dyed pieces.

Cotton pieces may be dyed :—

(1) In the Jigger.
(2) In the padding machine.
(3) In the winch machine.

Dyeing in the Jiggers.—The jigger is generally used in the dyeing of dark shades on cotton pieces, as the dyebath may be kept more concentrated owing to the small quantity of liquor used in proportion to the weight of the goods to be dyed. When heavy drills and similar materials are to be dyed the use of a jigger with nip rollers attached is strongly recommended, as the colour is driven into the fibre by the pressure of the squeezing rollers.

For light shades the bath is prepared with—

Quarter to half ounce soap or soda ash per gallon of liquor together with half the necessary quantity of dyestuff. The goods are given one end at a temperature of 140–160° F. (60–70° C.); the remainder of the colour is then added, and the pieces are run from one roller to the other till the desired shade is obtained, the bath being taken up to the boil. For medium shades the bath is charged with—

¼ oz. soda ash
2–4 oz. Glauber's salt or common salt
per gallon of liquor.

And for dark shades with—

¼ oz. soda ash
4–6 oz. Glauber's salt or common salt
per gallon of liquor.

When dyeing medium and dark shades it is advisable to add the soda ash and colour first, adding the Glauber's salt gradually towards the close of the operation. The levelling of the colour is thereby much facilitated. Care should be taken not to add excess of salt when dyeing in the jigger; this may be prevented by the use of the hydrometer. The bath (cold) should stand at 6-8° Tw. when dyeing dark shades.

Dyeing Cotton Piece Goods with Direct Cotton Colours in the Padding Machine.—The padding machine is chiefly employed for dyeing pale and medium shades on thin materials such as are used for linings. The trough of the machine usually has a capacity of 15–25 gallons, and should be heated by a steam coil if possible. The temperature of the dyebath should be from 130–140° F. (55–60° C.) for light shades and 160–212° F. (70–100° C.) for heavy shades.

The bath is charged with—

15–25 gallons water.
3–5 oz. soda ash.
½–1½ lbs. common salt or Glauber's salt.

About half the necessary amounts of soda ash, salt, colour, etc., are added, and the pieces are given one end. The remaining dye-solution, salt, etc., are added gradually after each end till the desired shade is obtained. When dyeing materials which are difficult to penetrate, it is advantageous to add ¼–½ pint of oleine oil and ¼–½ lb. dextrine to the dye liquor.

Dyeing of Cotton Pieces with Direct Cotton Colours in the Winch Machine.—This method is sometimes employed for strong and broad width materials, such as corduroys, velveteens, etc., the pile of which might be injured by dyeing in the jigger. The shades produced by dyeing in the winch machine are somewhat brighter than those obtained in the jigger.

The goods are dyed with the addition of—

2–4 per cent. soda ash.
10–20 per cent. Glauber's salt or } Calculated on the weight
20–30 per cent. common salt } of the pieces.

When dyeing in the winch machine there is no fear of the pieces being ended, though they are more likely to be creased and more colour is required than when the jigger is used.

Dyeing of Mercerized Cotton.—It may be stated in general that mercerized cotton is dyed with the same colours and in the same way as ordinary cotton save for the two following reservations :—

(*a*) **Owing to the increased affinity for direct cotton colours given to cotton by mercerization, less** colour is required to yield the same depth of **shade** than when dyeing ordinary cotton, also **less** assistant is required and more care is expended in dyeing it, *i.e.* the dyeing is carried out more slowly. For instance, more liquor is usually taken than for ordinary cotton, whilst the temperature is raised more slowly. Light shades are frequently dyed in a soap bath without any other addition, and wrung out and dried without washing. This entails the use of a little more colour, but that is quite negligible compared with the risk of a batch of goods being uneven.

(*b*) When the cotton is scrooped after dyeing care must be taken to avoid colours whose shade will be altered by the acid used in the scrooping.

Scrooping of Mercerized Cotton.—To obtain a scroop on mercerized cotton the goods are worked 10–20 minutes in a cold bath containing 10 per cent. soap; they are then wrung out or hydroextracted without rinsing, and worked 10 minutes in a cold bath containing 1–1½ oz. acetic acid per gallon. The scroop so obtained is not so permanent as that which is obtained if tartaric acid (which is, however, more expensive) is substituted for acetic acid. When using tartaric acid one-third of the above quantity of acetic acid only should be taken. If the goods are dyed in a strong soap bath, wrung out without rinsing and worked in a cold acid bath, the same effect is obtained.

Machine Dyeing.—Machine dyeing for loose cotton, sliver, beams, cheeses, cops, and hanks is increasing rapidly owing to the improvement of the various machines, the number of which prevents the giving of detailed instructions except on the following two points :—

(*a*) Use should only be made of colours which are easily soluble and possess good penetrating powers so that the goods are properly dyed through.

(*b*) Owing to the liquor usually being a short one, less common salt or Glauber's salt is needed in order to exhaust the bath; moreover, this should be gradually added after the material has been thoroughly saturated with the dye liquor, so that the colour is not flushed on to the outside of the material when the assistant is added.

The Aftertreatment of Direct Cotton Dyestuffs.—Experience has shown that the methods of aftertreatment detailed hereafter are of great utility in improving to a remarkable extent the fastness of some direct cotton dyestuffs to light and washing. It cannot, however, be overemphasized that the methods are not applicable to all members of this class, but only to certain of them which are fully specified in the various colour-makers' literature. Aftertreatment with bichrome is only really effective with dyestuffs which contain salicylic acid, like diamine green G and chlorazol brown M.

It must always be remembered that the shade of the dyestuffs is more or less altered by the aftertreatment. Sky blue FF when aftertreated with copper sulphate is changed much greener. Aftertreatment with formaldehyde is the most recent method to be adopted, and was receiving considerable attention at the hands of the colour manufacturers just prior to the war. It is one of the most promising methods, because it has very little effect on the shade whilst improving the fastness to washing to a remarkable extent. The colours which are suitable are those which have in their end component two hydroxyl or two amido groups in the meta position, such as many direct cotton blacks which have meta phenylene diamine as one of the end components. A complex condensation takes place between the amido or hydroxyl groups and the formaldehyde, which condensation products are insoluble and are therefore faster to washing and not so liable to stain adjacent white.

Aftertreatment with Copper Sulphate.—This process improves to a remarkable degree the fastness to light of those dyestuffs which are suitable. A fresh dyebath is charged with ½–1 per cent. copper sulphate, in which the well-washed dyed material is worked 20–30 minutes at 140° F. (60° C.). In connection with this process it must be remembered that a severe alkaline washing removes the effect of the copper sulphate to a great extent, whilst in some cases washing alters the shade considerably. Direct cotton blues and browns are largely put through this process, especially the FF sky blues and the RW direct blues.

Aftertreatment with Chromium Fluoride or Bichrome.—This process considerably improves the fastness to washing and milling but not to light of those dyestuffs which are suitable. A fresh dyebath is charged with 1–4 per cent. chromium fluoride or 1–2 per cent. bichrome, in which the well-washed dyed cotton is worked 20–30 minutes just below the boil. Bichrome has a more marked effect on the shade than chromium fluoride.

Aftertreatment with Bichrome plus Copper Sulphate.—In order to improve the fastness of the colours to light and milling in one operation it is common practice to work the dyed cotton for 30 minutes at 195° F. (90° C.) in a fresh bath charged with ½–2 per cent. bichrome, ½–2 per cent. copper sulphate, and 1–2 per cent. acetic acid. Any cloudiness in the bath must be corrected by addition of more acetic acid before entering the cotton.

Aftertreatment with Formaldehyde.—This process has a marked effect on the fastness to washing and milling but not light of those dyestuffs which are suitable. A fresh bath is charged with 1–3 per cent. formaldehyde (40 per cent.) in which the cotton is worked 20–30 minutes at 140° F. (60° C.). This process is of especial value for most direct cotton blacks, whereby the fastness to washing against white cotton is remarkably increased.

Coupling with Diazotized Paranitraniline.—This process really amounts to the making of a new colour on the fibre, as is evidenced by the increased density of the shade in the case of blacks, whilst with many other colours the coupled shade is completely different to the dyed shade, which makes the exact matching of a shade very difficult. The coupled colour is faster to washing and acids than the coupled colour, but no improvement is made in the fastness to light. It requires some little experience to diazotize paranitraniline, but the following method will be found to give a perfectly clear solution with a little practice. Diazotized paranitraniline may be prepared as follows: 2 lbs. paranitraniline are stirred into a paste with 3 gallons boiling water, then 5½ lbs. spirits of salt 32° Tw. are added, and the mixture stirred until it goes clear. If it does not go clear the solution must be boiled, because it is essential, for complete diazotization that the solution is clear when the cold water is added. 10 gallons of cold water is now slowly added during continuous stirring, the object of which is to get the paranitraniline precipitated in as fine a state of division as possible—the finer the state of division the easier to diazotize. This is allowed to cool, then 1 lb. nitrite of soda (98 per cent.), dissolved in 2 gallons cold water, is added all at once, and the solution stirred till it goes clear. On adding 4½ gallons water to the above one has a 1 per cent. solution of diazotized paranitraniline from which any given weight may be easily measured. The diazotized paranitraniline should be kept in the coolest place in the dyehouse. For every gallon of the above solution added to the dyebath, add 1¼ oz. soda ash and ¾ oz. sodium acetate. The object of this addition is to neutralize the hydrochloric acid and to have acetic acid present. Coupling will not take place in presence of hydrochloric acid, so that it is partially neutralized with the soda ash, then the balance is neutralized with sodium acetate, which sets free acetic acid. Partial neutralization with soda ash is made to economize the use of the more expensive sodium acetate. Basic colours may be added direct to the coupling bath, by which means the beauty of the shade may be considerably enhanced. Blacks are frequently beautified by addition of 0·1 per cent. methylene blue B to the coupling bath. Coupling is carried out in a fresh bath for half an hour.

DIRECT COTTON DYESTUFFS (WHICH MAY BE DIAZOTIZED AND DEVELOPED).

The first member of the direct cotton dyestuffs which could be diazotized and developed was discovered by Green in 188[illegible], to which he gave the name Primuline. This colour had no special interest as a direct cotton dyestuff owing to its fugitiveness to light. It was, however, discovered that, owing to the presence of a free amido group, it could be diazotized and developed; by combining it with various amines and phenols a range of yellow, orange, red and maroon shades could be obtained of very good fastness to milling, washing and boiling acids. This operation can be carried out by first dyeing the cotton with a diazotizable colour, then diazotizing and developing on the fibre. These good properties gradually—because novel methods of application have to gain the confidence of dyers by proving themselves in the manifold uses to which the different classes of goods are subjected—led to the adoption of this process, and primuline red (primuline $+\beta$ naphthol) became a standard shade. As usual when a new departure in colour chemistry is discovered it is exhaustively worked by colour chemists, with the result that there is now a large number of diazo dyestuffs available, some of which have outstripped primuline in importance. The most successful have been the BH type of black, diaminogene B and Zambesi blacks, the consumption of which has been enormous for sewing thread and mercerized yarns. The dyeing process is a complicated one as will be seen below, so that when the sulphur blacks were introduced developed blacks began to lose their importance except for certain lines such as sewing threads, because a much faster black could be obtained with sulphur blacks in a much simpler manner. Owing to the lack of a sulphur red, developed reds have still held their own where reds fast to boiling acids, milling, crabbing, etc., are required. One weak point of this class of colour has been the poor fastness to light, but the latest additions to this class of colour—diazo fast scarlets—have shown a welcome improvement in this respect. The improved fastness of the developed dyestuffs as compared with direct cotton dyestuffs is due to the fact that the colour which is produced on the fibre is insoluble in comparison with the same colour before it is developed. It is only to be expected that the colour is faster to washing, etc., because the more insoluble a cotton dyestuff is, the faster it is as a general rule.

The main points to remember in connection with this process are:—

(1) Stone or wooden vats must be used for diazotizing: on no account may iron cisterns be used, or else the diazo compound is destroyed.

(2) The diazotized compound is sensitive both to light and heat, either of which decomposes it, so that no delay whatsoever must take place in developing the goods after diazotization has taken place. No sunlight must be allowed to play on the cotton, nor must it be put close to a stove or hot steam pipe, because cotton so exposed will not subsequently develop.

(3) Except with naphthylamine ether and amido-diphenylamine all developing baths should be on the alkaline side, or else the shade will not develop properly.

The cotton is dyed in the manner described in the earlier part of this section: it is then well washed and worked 15–30 minutes in a cold bath, charged with 1–3 per cent. sodium nitrite, 5–10 per cent. spirits of salts, or 3–5 per cent. sulphuric acid. The cotton is lightly rinsed and passed without delay into the cold developing bath, in which the material is worked 15–30 minutes, after which the cotton is washed, soaped if thought desirable, and dried.

The following developers are the most commonly used: Resorcine, meta phenylene diamine, meta toluylene diamine and β naphthol: naphthylamine ether and amido-diphenylamine are used for blue shades, whilst phenol and α naphthol are occasionally used. With the exception of naphthylamine ether and amido-di-phenylamine, which require to be dissolved with their own weight of spirits of salts, the above developers are dissolved by stirring them into a smooth paste with their own weight of caustic soda, and pouring boiling water over them. With the above two exceptions, all the developers are miscible one with the other in any proportion. This is frequently done, because in the case of blacks meta phenylene diamine gives a black with a brownish cast which may be corrected by the use of some resorcine which gives a green tone black, or B naphthol which gives a blue tone black.

Wool.—A few direct cotton dyestuffs give shades of excellent fastness to washing and milling on wool, whilst the fastness to light is generally much better than the same colour on cotton. They, therefore, find a limited use in wool-dyeing, *e.g.* the shawl trade, effect threads in woollen pieces, knitting yarns, etc., whilst a colour like benzopurpurine 4B is largely used as a scarlet in the low woollen trade. It must, however, be remembered that the majority of direct cotton dyestuffs will stain any cotton washed with any wool dyed with them. In dyeing these colours prepare a dyebath with the requisite amount of colour and 10–20 per cent. common or Glauber's salt. Enter the wool lukewarm, raise to boil and dye boiling 1 hour. To facilitate exhaustion of the dyebath acetic acid may be added, except with benzopurpurine and similar colours sensitive to acid. When afterchroming with chromium fluoride this is added to the dyebath after the bath has been exhausted with acid and boiling continued another ½ hour.

The types most commonly used are chrysophenine G, owing to its fine shade, fastness to washing and excellent fastness to light; benzopurpurine 4B; deltapurpurine 5B; reds of the diamine fast red F type, owing to their excellent fastness to light and milling, coupled with the fact that they may be used with mordant dyestuffs, since they are salicylic acid compounds: the same reason applies to direct greens of the chlorazol green G type.

Silk.—The direct cotton dyestuffs are of great utility in the dyeing of silk when shades fast to milling, washing or water are required, whilst selected diazo colours give shades of good fastness to boiling soap, *e.g.* primuline developed with β naphthol is largely used on silk for a red fast to soap, whilst diazo blacks are used to dye a fast to milling black on silk noils, which is a form of silk very difficult to dye in fast shades.

Application.—Dye in a boiled-off liquor or soap bath with the addition of 10–40 per cent. Glauber's salt. Enter lukewarm, bring the bath gradually to the boil and dye simmering ½ hour. In a large number of cases acetic acid, and even sulphuric acid may be added to get exhaustion of the bath. This must be avoided if the colour is sensitive to acids, for the same reason scrooping must be used with discretion.

All the methods of aftertreatment detailed above for cotton may be used on silk, whilst the developed dyestuffs are dyed in the same way.

GENERAL NOTES.

The direct cotton dyestuffs are applied to linen and jute in exactly the same way as detailed for cotton. They are used on linen very largely, whilst on jute they are used for special lines where an improved fastness is required.

A basic dyestuff forms a precipitate with a direct cotton dyestuff when mixed together, which shows that they have an affinity for one another. They must, therefore, never be used in the same dyebath. Advantage is, however, taken of this affinity in topping direct cotton dyestuffs with basic dyestuffs. Topping with a small amount of basic dyestuffs has a very beautifying effect on the shade. It is very common practice to top direct cotton blacks with 0·1 per cent. methylene blue 2B, which counteracts any redness of tone. The topping is carried out in a cold bath, charged with the requisite colour and 1–2 per cent. acetic acid. Enter cold, work cold 10 minutes, then raise up to 140° F. (60° C.) in [illegible] minutes. The acetic acid is used to prevent the colour striking on too quickly, but must not be used in cases where the direct cotton colour is sensitive to acids. Discretion must be used in warming up the dyebath, because in many instances this will not be necessary, as the colour will exhaust cold.

The direct cotton dyestuffs are not used in dyeing vegetable-tanned leather owing to lack of affinity, but they are gaining increased importance in the dyeing of chrome-tanned leather for which they have good affinity.

Dyeing is usually carried out in the drum in which the leather is first drummed with borax in order to remove any acid which may be left in the skin from the tanning process. The leather is then drummed for ½ hour at 100° F. (40° C.) with the requisite dyestuff, with or without the addition of Glauber's salt. Large quantities of direct cotton blacks of the chlorazol black E type are used for dyeing chrome leather black.

Wood chip is largely dyed with direct cotton dyestuffs, for which it has a good affinity. Dyeing is carried out at the boil with the addition of Glauber's salt or common salt, until the plait is sufficiently penetrated.

Selected direct cotton dyestuffs of good fastness to light are used in the paper trade for shades in which fastness to light is required. Stilbene yellows are largely used on paper, also direct cotton pinks.

SECTION VI.—THE AZOIC OR INSOLUBLE AZO COLOURS

AZOIC is the distinguishing name given to that class of azo dyestuffs which are not applied as dyestuffs, but are actually produced within the fibre by impregnating the fibre with one component of the colour, followed by a passage through the diazo solution of the other component: since ice is beneficial in preparing the diazo solution of the respective amine or diamine employed, this class of dyestuffs is also known as ice colours. It will be gathered from the above that the application of these colours is not a dyeing process, but is actually direct-colour formation on the fibre. Similar to the manufacture of azo dyestuffs on the big scale the process is carried out cold. This process was first patented in 1880 by Messrs. Thomas and Robert Holliday, who did a large business in this class of colour, chiefly in vacanceine red: this was produced by coupling β naphthol padded yarn with diazotized β naphthylamine, which yielded a fine blue-red which was largely used in towelling. In the first patent the advantage of previously preparing the cotton with oil was not included, but this was subsequently patented in 1882. Moreover, unlike para red on yarn, vacanceine red was both prepared and developed in 100-lb. lots, whereas para red is done in 2-lb. lots.

The most popular combination in this class of colour is β naphthol + paranitraniline, which is a fine red commercially known as para red. On pieces it is produced in enormous quantities as a cheap substitute for Turkey red, but on yarn it is applied to nothing like the same extent. Paranitraniline was first produced in 1889 by Meister, Lucius and Brüning, who have played the leading part in the development of this class of colour. Paranitraniline was particularly well received in Russia, and Russian chemists have played a prominent part in the adaptation of this process to calico printing (in which it is most largely used), especially in the successful discharging of the same.

Alpha naphthylamine + β naphthol gives a claret which may be classed as the second most popular azoic colour. It is used extensively on pieces, but nothing like to the same extent as para red, and to a very limited extent on yarn. In 1893 dianisidine was introduced, which in combination with β naphthol gives an unattractive blue of a dull violet hue, not fast to light; if, however, the coupling is carried out in the presence of a copper salt, a fine shade of blue is obtained which is fast to soap and faster to light than indigo on cotton: it has, however, the drawback of not being fast to acids or perspiration, so that its adoption has not been as widespread as was at first anticipated.

β naphthol was practically the only body used for coupling with the various amines employed until naphthol AS was introduced, which is fully dealt with later in this section. A modification of β naphthol has been used under the name of naphthol R, which consists of a mixture of 9 pts. β naphthol with 1 pt β naphthol mono HSO_3 2 : 7. The admixture of this sulphonic acid makes the shade bluer than with β naphthol alone, but the presence of the sulphonic acid naturally makes the red produced more soluble and therefore less fast to soaping.

The following are the chief amines and diamines which have been used with β naphthol and the respective shades yielded by them :—

Paranitraniline.	Red.
α Naphthylamine.	Claret.
β Naphthylamine.	Blue red
Metanitraniline.	Orange.
Nitro Toluidine.	Orange.
Benzidine.	Puce.
Tolidine.	Puce.
Nitrophenetidine.	Pink.
Dianisidine (with Copper Salt).	Blue.

The properties of this class of colours are very good in that they possess very good fastness to washing and soaping, coupled with a fastness to light superior to the direct cotton dyestuffs. The shades are also fast to acids except the copper salts, which are sensitive to acids. This is the weakness of dianisidine blue, which is coupled in the presence of copper chloride. The shades also possess a good fastness to chlorine. The two defects of this class of colour are that they rub off to a greater or less extent according to the skill with which they are dyed: this can be easily understood when it is remembered that the process consists of precipitating an insoluble colour in the fibre, because there is bound to be precipitation on the surface. The degree of rubbing largely depends upon the thoroughness with which the soaping is carried out. The other defect is that the colours sublime off the fibre on heating. This defect is used as a characteristic test for this class of colour, viz. placing the pattern between white calico and ironing with a hot iron, when the colour will sublime on to the calico: shades which have been coppered or coupled in the presence of a copper salt do not sublime.

The production of these colours is carried out in the following way: The material is first padded with the β naphthol, dried, the colour developed by passing through the diazo solution, then washed, soaped, washed and dried.

β naphthol being insoluble in water, it is necessary to bring it into solution before the fibre is impregnated with it. This is done by use of caustic soda, which rules out the use of these colours for animal fibres. The following is a typical β naphthol prepare:—

2½ lbs. β naphthol

are stirred into a smooth paste with

½ pints caustic soda 90° Tw.,
7½ lbs. Turkey red oil,

which is then dissolved by pouring 9 gallons of boiling water over the paste whilst stirring.

The material must be thoroughly boiled out with alkali to clean it and then dried before being padded with the above solution. It will be readily understood that unless the material is padded evenly with the β naphthol the resulting shade will naturally be uneven when the para red is developed. The greatest care must therefore be taken in wringing out the yarn or squeezing the pieces. The sticks which are used for the yarn must be used for this purpose only, and should be saturated with the β naphthol prepare before being used. Yarn is usually padded 2 lbs. at a time, and automatically squeezed, fresh prepare being added to the bath to compensate for the amount taken out of the trough by the yarn. The yarn is then dried on revolving drying machines or hung on sticks in the stove. Pieces are padded on a padding machine, then dried in the hot flue or less frequently on drying cans. The drying of β naphthol prepared material has to be very carefully carried out, because the β naphthol sublimes off the fibre at high temperatures. Drying should, therefore, be carried out at 120–140° F. (50–60° C.). Once the padded material has been dried it should be developed as quickly as possible, because it turns brown on exposure, so that the resulting shade is not so bright. For the same reason no more padding-solution should be prepared than can be used in one day, because it also turns brown and deteriorates on keeping. Again, the greatest care must be exercised in handling the dry padded material. Wherever it is touched with a wet hand or a drop of water falls on it there will be a yellow mark when the shade is developed, due to the dissolving of the β naphthol by the moisture. This tendency to turn brown may be delayed by the addition of alkaline antimony oxide solution to the β naphthol prepare.

The padded material is passed through the solution of diazotized paranitraniline when the red develops practically instantaneously.

The perfect diazotization of paranitraniline requires a certain amount of skill and practice; if attention is paid to the following instructions a good result will be obtained :—

Two lbs. paranitraniline are stirred into a paste with 3 gallons boiling water, then 5½ lbs. spirits of salts, 32° Tw., are added, and the mixture stirred until it goes clear. If it does not go clear, the solution must be boiled until it does go clear. This is an essential point, because it is necessary for complete diazotization that the solution is clear when the cold water is added. Ten gallons of cold water are now added, whilst continuously stirring, the object of which is to get the paranitraniline hydrochloride precipitated in as fine a state of division as possible—the finer the state of division, the easier to diazotize. This is allowed to cool—if ice is available it should be used to cool the solution to 3–4° C. One lb. of sodium nitrite dissolved in 2 gallons of cold water is added all at once, and the solution stirred until it goes clear—it is essential to add the sodium nitrite all at once. On adding 4½ gallons cold water to the above one has a 1 per cent. solution of diazotized paranitraniline. If the diazo solution does not go clear on adding the nitrite, but a voluminous yellow precipitate is formed, this is a certain indication that there is a shortage of hydrochloric acid or sodium nitrite. Hydrochloric acid should always be present in excess, because it makes the diazo solution more stable. Sodium nitrite should also be present in excess to counterbalance any loss of nitrous fumes and to ensure all the paranitraniline being diazotized. Both these precautions prevent diazotized paranitraniline coupling with any unchanged paranitraniline present to form the voluminous yellow precipitate referred to above.

It will be gathered from the above that a method of avoiding the troublesome process of diazotizing paranitraniline would be a desirable thing and a commercial success. Since 1894 stable diazotized paranitranilines in powder form have been on the market. Though dearer to use than paranitraniline, they have been readily adopted where occasional use only was being made of the diazotized paranitraniline.

The first stable form of diazotized paranitraniline manufactured commercially was nitrosamine red, which was put on the market in 1894. This is represented by the formula $NO_2C_6H_4N\langle^{NO}_{Na}$, and is formed by the addition of caustic soda to diazotized paranitraniline, until it is alkaline. Great hopes were built on this product in that it was thought possible to print the β naphthol and nitrosamine red on the cotton together, and so produce para red in one process. Theoretically it was possible, but in practice it was not found possible to get good results. However, by an addition of hydrochloric acid to nitrosamine red diazotized paranitraniline is obtained so that it could be used as a stable form of diazotized paranitraniline. The two other stable forms of diazotized paranitraniline are sold as nitrazol C, put on the market in 1897, and azophor red PN, —the latter consists of diazotized paranitraniline and desiccated Glauber's salt or aluminium sulphate. The use of these stable forms of diazotized paranitraniline is very convenient, as it abolishes the necessity of ice, which is not always obtainable, but it should always be remembered that one pays for this convenience.

When developing para red two things must be remembered, viz. the developing bath must be dead cold and no mineral acid must be present in the coupling bath or else coupling cannot take place. The mineral acid is preferably neutralized by means of sodium acetate, which liberates acetic acid in neutralizing the hydrochloric acid. Since sodium acetate is expensive part of the mineral acid is neutralized with caustic soda or soda ash, the neutralization completed with sodium acetate. The developing solution of diazotized paranitraniline (prepared as detailed above) is diluted with 1 gallon of cold water, in which 1¼ oz. soda ash and ¾ oz. of sodium acetate have been dissolved for every gallon of diazotized paranitraniline.

A developing bath of azophor red PN is prepared as follows :—

> 33½ lbs. azophor red PN are made into a smooth paste with 20 gals. cold water : after standing for several hours the clear liquid is drawn off : the residue is washed with

7 gals. water and the clear solution again drawn off. Then
17¾ lbs. caustic soda, 36° Tw., diluted with
6 gals. water, is added.

The developing solution, once it has been neutralized, must be used straight away, because in this form it is not stable.

Yarn is worked in the developing bath 2 lbs. at a time, and after being wrung out, is allowed to lie for some time before washing in order to ensure that the coupling is complete.

Pieces are developed on the padding machine and given an air passage before passing to the washer in order to complete the coupling.

The developed material is thoroughly washed, then thoroughly soaped for 15 minutes at 140° F. (60° C.), with ½ lb. soap per 10 gallons. If alkali is added the shade is turned bluer. On the thoroughness of the soaping depends the fastness to rubbing: if the temperature of the soap bath is taken higher than 140° F. (60° C.), the shade becomes yellower. The material is finally well washed and dried at a low temperature.

a **Naphthylamine Claret.**—This shade is produced on similar lines to para red, and the same precautions should be taken. The cotton is prepared with—

2½ lbs. *β* naphthol,
1½ pints caustic soda, 90° Tw.,
7½ lbs. gum tragacanth, 10 oz. per gallon,
made up with water to 10 gallons,

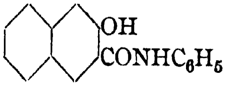
and developed in the following solution :—

9½ oz. *a* naphthylamine are dissolved with
5 quarts hot water and
1¼ noggins hydrochloric acid, 36° Tw. When cool add
2½ noggins hydrochloric acid, 36° Tw.,
8 lbs. ice ; and at 32° F. (0° C.) add
3¼ noggins sodium nitrite (3 lbs. per gallon).

The whole is then filtered and neutralized just before use with

20 oz. sodium acetate and made up with cold water to
4 gallons.

In 1912 the Chemische Fabrik Greisheim Elektron introduced a new naphthol which they termed naphthol AS, which is β oxy naphthoic acid anilide—



This has several advantages over β naphthol, as will be indicated later, but its initial high price prevented it from being a serious competitor of β naphthol, but no doubt the price will gradually be reduced. The war, of course, cut off supplies, but it had aroused great interest during the short time it had been on the market, owing to the brilliancy and fastness of the shades obtained coupled with the less stringent conditions required in applying it. For instance, the blue obtained by coupling dianisidine in the presence of copper chloride with naphthol AS, is claimed to be faster to chlorine than indigo or hydron blue. The red obtained by coupling fast red G base with naphthol AS is claimed to be faster to light than para red.

The great advantage of naphthol AS over β naphthol is that owing to the substantive dyeing qualities of naphthol AS as compared with β naphthol it is not necessary to dry the naphthol prepared material, but it may be passed straight into the developing bath after well squeezing it out of the naphthol bath. Another difference is the addition of formaldehyde to the naphthol bath, which permits of the impregnated cotton being allowed to remain wet, so that a large quantity may be prepared, then dyed altogether, instead of 2 lbs. at a time. Partial drying of the material must, of course, be avoided.

The following recipe is abstracted from the maker's pattern card :—

Naphthol AS prepare,
Naphthol AS, 120 grs.
Caustic soda, 62° Tw., 200 c.c.
Turkey red oil, 300 grs.

Stir the naphthol AS into a smooth paste with the caustic soda and Turkey red oil, then add some water and boil until dissolved, now make up to 10 litres, and add 120 grs. formaldehyde (40 per cent. solution). Impregnate the cotton at 80–100° F. (25–40° C.). On no account must the formaldehyde be added to the boiling bath, but only when it has cooled.

The cotton yarn should be boiled out with alkali and dried previous to impregnation; give 3–4 turns in the naphthol bath, wring out, pass through the bath again, wring out and straighten the yarn by dumping on a peg. Enter the wet yarn in the dyebath prepared as follows:—

Stir into a paste—

300 grs. fast scarlet G base with
600 c.c. hydrochloric acid, 32° Tw.: dissolve in
2000 c.c. boiling water: allow to cool, then add
1500 grs. ice.

Pour slowly into the above whilst stirring—

156 grs. sodium nitrite dissolved in
500 c.c. water.

Finally make up to 10 litres with cold water.

The actual dyebath is made up by mixing—

10 litres of the above diazo solution, filtered through calico with
10 litres cold water, and immediately before dyeing add
1600 c.c. acetate of soda solution, 1 : 1.

To replenish the bath as the liquor is taken up by the yarn passed through it, add ¾ litre per 2 lbs. yarn of the following diazo solution:—

10 litres diazo solution,
5 litres water,
1600 c.c. acetate of soda solution, 1 : 1.

After dyeing wash well, soap at 140° F. (60° C.), wash and dry at low temperatures.

Other bases for use with naphthol AS are put on the market; for further details the reader is referred to *J.S.D.C.*, April, 1914.

In February, 1916, a further improvement was announced in the application of naphthol AS. The author gives the details, but is not in a position to endorse or otherwise the claims made. It has been found, and patented in November, 1914, by the Griesheim Elektron, that concentrated solutions of nitrosamines made from the bases recommended by them and naphthol AS alkali salt are stable, and may be obtained in paste or powder form without formation of the colour. The above are pale yellow in colour, and dissolve easily in cold water. Dilute solutions of the above precipitate the respective dyestuffs, if warmed, or if acetic acid or bichrome is added. On the other hand, the addition of monochromate to the solutions increases the stability. The presence of alkali also increases the stability, as one would expect.

These stable mixtures of nitrosamine alkali salt and naphthol AS are put on the market under the name of "Rapid Fast Dyes."

The following illustrates the method of procedure in piece dyeing :—

150 grs. rapid fast dye red GL paste are mixed with
360 c.c. cold water,
40 c.c. Turkey red oil, and then
500 c.c. cold water is stirred in.

The cloth is padded with this mixing, dried in the hot flue or hanging stove, then passed through a solution containing 40 c.c. acetic acid, 8° Bé., and 75 gr. Glauber's salt per litre, which is kept just under the boil. The bath must remain acid whilst the cloth is passing through : to this end the bath must be tested for acid, and more added if necessary. The cloth is then well washed, soaped as usual for these colours, washed and dried.

It is claimed that the results are practically equal to those obtained by first padding and then developing. If practical experience confirms these claims, then it is evident that this process is of a far-reaching importance which it is difficult to estimate.

SECTION VII.—THE RESORCINE DYESTUFFS

THE resorcine or phthaleine dyestuffs necessitate a section to themselves owing to the fact that they include colours which are used as basic, acid, and mordant dyestuffs in the dyeing industry. However, the methods employed in their application are identical with those detailed in the respective sections.

Included in this group of dyestuffs are eosines, rose bengal, erythrosine, phloxine, which give a beautiful range of pinks on silk and wool, and are also applied by a special process to cotton. Eosines are also used for the manufacture of imitation vermilion lakes and red ink. The rhodamines are applied both as basic dyestuffs on cotton, acid dyestuffs on silk and wool, and are also used on jute, paper, leather, straw, wood chip, etc. Fast acid violet A2R, violamine, etc., are applied as acid dyestuffs to silk and wool, and yield red violet shades of good fastness to light and milling. Finally, galleine and cœruleine are applied as mordant dyestuffs on wool and silk and are also used in calico printing fixed with acetate of chrome.

The first member of this group was fluoresceine, which was discovered in 1871. It was never largely used as a dyestuff, but was interesting owing to the fact that it gave a fluorescent solution in water, which is characteristic of many of the eosines and rhodamines. The eosines followed from 1874 onwards, succeeded by rhodamine B in 1887. This group of dyestuffs includes indisputably the most brilliant and beautiful coal tar dyestuffs extant, and in their early days fetched very high prices, until competition brought them down to remarkably low figures.

The fastness to light of these colours is not remarkable, but the shades have become standard in many sections of the dyeing trade, and the merchants recognize that if they will have the bright shade they must accept the poor resistance to light as well. The fastness to washing is also not good as a rule, but rhodamine B,G and fast acid violet A2R are quite good to washing and light milling on wool, whilst galleine and cœruleine will withstand a severe milling when used on chrome mordanted wool. The consumption is relatively large.

Their application requires very little space. Eosines are applied on cotton in the following way : Make up a bath with salt to stand at 7° Tw., and add the dissolved colour to this. The cotton is dyed lukewarm, steeped for 1–2 hours, and dried without rinsing. The rhodamines and eosines are dyed like acid dyestuffs on wool and silk, though the eosines are now practically never used on wool. It should here be mentioned that rhodamine B or G in combination with acid orange II. yield very bright scarlets, which are brighter than may be obtained with homogeneous acid scarlets. On jute this combination has the drawback that the rhodamine does not penetrate as well as the orange so that the centre of the jute yarn dyed with this combination is orange instead of scarlet.

On cotton the rhodamines are applied like basic dyestuffs, rhodamine 6G being the universal type for cotton, because rhodamine B or G do not yield pleasing shades on this fibre. Less tannic acid is required by the rhodamines as a mordant than by the other basic dyestuffs.

SECTION VIII.—THE SULPHUR DYESTUFFS

THE earliest known type of this class of dyestuffs was cachou de laval, which was discovered by Croissant and Bretonniere in 1873. Although it possessed properties of great value to the cotton dyer, it remained the sole representative of this class of dyestuff until Raymond Vidal—a French chemist—discovered Vidal black in 1893. This dyestuff was at once novel in its application and outstanding in its properties of fastness to light, milling and washing, and boiling acids—far surpassing any cotton black known to cotton dyers with the exception of aniline black produced on the fibre by the oxidation of aniline oil or salts. Vidal's discovery aroused the greatest interest, both in colour-making and dyeing circles, with the natural result that the fusion of organic bases with caustic soda and sulphur, etc., was so intensively and successfully worked that the consumption of sulphur dyestuffs is now extremely large. The range of this class of dyestuffs include blacks, blues, greens, browns, oranges, and yellows. There are, however, some notable gaps in the series before the range may be considered complete. At the time of writing no bright scarlet, crimson, or violet has been commercially produced belonging to the sulphur dyestuffs.

It is a curious fact that, if the first representative of a new class of dyestuffs is of exceptional fastness, the conclusion is jumped at that all members of this class possess the same exceptional fastness, and it is only by bitter experience that colours are estimated at their true value. This mistake was made in the case of the sulphur dyestuffs, and has been repeated in recent years in the case of the vat dyestuffs, which latter class, though it contains some of the fastest dyestuffs known, also includes dyestuffs which are not even fast to cold water. It must always be remembered that there are considerable variations in the fastness to light of the different sulphur dyestuffs. With few exceptions no sulphur dyestuff is as fast as the sulphur blacks; some sulphur blues and some sulphur greens—such as cross dye green B—possess similar fastness, but sulphur browns, olives, and oranges cannot be compared with the sulphur blacks for fastness to light, whilst the sulphur yellows are notably deficient in fastness to light. To overcome this deficiency of the yellows it is a very common and commendable practice of dyers to use a direct cotton yellow of the chlorazol fast yellow B type. Such yellows possess excellent fastness to light—infinitely superior to sulphur yellows—coupled with very good fastness to milling and washing, so that their use is permissible and advisable except when the dyed shade has to withstand a subsequent boiling with acid, *e.g.* cotton warps which are cross-dyed. The type of direct cotton yellow mentioned will withstand the reducing action of the sodium sulphide, but it must be remembered that the majority of direct cotton dyestuffs will not do so, but are destroyed. It must also be noted that the sulphur dyestuffs will not stand the action of chlorine, but are peculiarly sensitive to it.

The virtues of the sulphur dyestuffs immediately forced themselves on the notice of the dyers, but the method of their application was so novel that they were looked upon with diffidence. Some of the earliest results of their application on the big scale were weird in the extreme, and very discouraging, but the early difficulties of their application were, however, gradually overcome with the co-operation of the master dyers. Nowadays the dyeing of sulphur dyestuffs is thoroughly understood, and few difficulties are encountered.

Side by side with the improvement of the methods of application must be recorded improvements in the methods of manufacture, notably in the case of the blacks. The earliest types of sulphur blacks, such as Vidal black, possessed much inferior colouring power and affinity for the cotton, compared with the modern types; moreover, one had to chrome the cotton after dyeing in order to fully develop the shade. Modern sulphur blacks do not, however, require chroming, and indeed are practically never chromed except in the case of warps. In the early days of sulphur dyestuffs their application was strictly confined to vegetable fibres; silk and wool could not be dyed owing to the strongly alkaline nature of the dyebath. In the case of cotton their use was confined to raw cotton, hanks and warps owing to the rapidity with which the earlier types oxidized, which made the level dyeing of pieces impossible due to the selvedges bronzing so quickly. Nowadays an enormous number of cotton pieces are dyed in the ordinary jigger without any trouble in the ordinary routine of the cotton piece dyehouse.

Several processes have been patented for the dyeing of silk, wool, and mixed goods. On silk they may prove useful for shades fast to boiling, but I am of opinion that there is practically no scope for their application on all wool goods because of the large number of satisfactorily fast wool colours which are available: colours which are not only faster than the average sulphur dyestuffs, but whose application is easier and which leave the wool in better condition. For instance, there is no comparison in the ease of dyeing a worsted piece with diamond black compared with dyeing a similar piece with sulphur black. On silk they may prove useful for shades fast to boiling soap, but their general lack of brightness will prove a drawback for this class of work. In union dyeing I can see every prospect of success for certain classes of work—these are fully detailed in Section X.

One great drawback to the earlier sulphur blacks was the tendering of the cotton due to the development of sulphuric acid on storing. A large amount of work has been done on this subject, and the conditions which favour tendering and those which retard tendering have been determined, so that cotton dyers know what to avoid and when not to use sulphur dyestuffs.

Experience has shown that goods which have subsequently to be stoved, *i.e.* bleached by means of sulphur dioxide, must not contain any material dyed with sulphur blacks. This process accelerates tendering to a surprising degree. Dyers are, therefore, accustomed to use direct cotton colours developed for this purpose.

Experience has shown, also, that sulphur blacks after-treated with copper sulphate are very liable to tendering, so that it should never be used. This is to be regretted, since an after-treatment with copper sulphate beautifies the shade of many sulphur blacks. Investigations have also shown that a subsequent aftertreatment with bichrome is beneficial in reducing the danger of tendering. Warps are still very frequently chromed, because when using a twelve-box machine a chrome box involves very little extra trouble. The reader naturally asks, How can one quickly test a specific dyeing for liability to tender? This may be simply carried out as follows on the lines of the stability test for artificial silk : Heat the cotton in a stove for 1 hour at 140° C., remove, expose to the atmosphere till the cotton has regained its natural moisture, then repeat the process. It is always advisable to heat at the same time a piece of the cotton undyed as a blank test in order to see that the cotton itself does not deteriorate under the conditions of the test. Too much stress cannot be laid on the fact that it is absolutely essential that the breaking strain tests of the various cottons tested should all contain the same amount of moisture. This is obtained by allowing all the various cottons to be hung side by side for 12–24 hours previous to taking the breaking strain.

The following is abstracted from the published work of Dr. Zanker and collaborators dealing with a long series of experiments conducted with a view to throw light on the causes of the tendering of sulphur black dyed cotton. The first experiments were carried out in 1913, and further results have been published at intervals since then. The author considers the work to be a valuable contribution to the research already carried out by other investigators.

The method recommended for determining whether a sulphur black will tender or not is carried out as follows:—

Dyed samples of equal depth are heated for one hour in an oven at 140° C. The hank is then taken out and allowed to lie in the atmosphere till it has taken up the normal amount of moisture. It is then re-heated for a farther hour to 140° C., taken out and tested.

It is essential to carry out the work in the manner described because the moisture of the atmosphere plays a definite part in helping the tendering. In every heat test a blank experiment should be made with undyed cotton yarn; this should be heated at the same time in order to make certain that no tendering of the cotton is caused by the high temperature alone. The progressive rate of tendering is indicated in the following table, and shows the action of temperature in promoting tendering. The same dyeing exposed to the given temperatures took the stated lengths of time to reach the same state of tendering.

Ordinary Room Temperature	1½ year.
40–50° C.	10 months.
60° C.	4 ,,
80° C.	1 month.
100° C.	72 hours.
120° C.	31 ,,
140° C.	2 ,,
160° C.	1½ hour

In every case free sulphuric acid could be found in the cotton.

The above method of testing has been in use since January, 1907, and since that date has been found to give reliable tests as to the liability of any special sulphur black to cause tendering.

The sulphuric acid did not arise from any free sulphur which might have fastened itself on to the fibre, because all yarns before testing were extracted with carbon bisulphide in order to remove all the free sulphur.

The following method is used to determine the amount of total sulphur present in any sulphur black :—

Two and a half grams of the material to be tested are put in a beaker with 75 c.c. of bleaching liquor at 2° B., completely free from sulphate. The cotton is left in this liquor until it is bleached completely white, then squeezed out and immersed in a further 50 c.c. of bleaching liquor for one hour at 30–40° C. By this means the last trace of sulphur is quantitatively converted into sulphuric acid. The cotton is then washed five times with boiling distilled water, and the washings added to the bleaching liquor. The total liquor is then evaporated down and acidified with pure hydrochloric acid and the solution boiled in order to get rid of all the chlorine. The sulphuric acid is then precipitated by the addition of barium chloride.

The following results were obtained by four different estimations of one and the same dyed material :—

Determination.	S calculated as SO_3.	S calculated as sulphur.
1.	2·56	1·023
2.	2·67	1·070
3.	2·65	1·068
4.	2·59	1·031

The quantitative estimation of the formation of sulphuric acid in a sulphur black dyeing was carried out as follows :—

The material was heated for two hours at 140° C. according to the method already described, when it was found that the formation of sulphuric acid, even after heating one hour, was so considerable as to cause the yarn to depreciate 65 per cent. in its breaking strength. After the cotton had been heated as above, it was put into an excess of caustic soda liquor 1/100 normal. The caustic soda liquor was then titrated back and the amount of sulphuric acid was thus determined.

As a control experiment the sulphuric acid formed was also determined by precipitation with barium chloride. The figures were found to agree with the caustic soda method.

By this method the following tables were reached :—

Determination.	S calculated as sulphur.
1.	0·223
2.	0·227
3.	0·229
4.	0·227

The amount of unchanged sulphur still left on the fibre was then determined by the bleaching liquor method already detailed.

Determination.	S calculated as sulphur.
1.	0·742
2.	0·700
3.	0·731
4.	0·743

To show how close the total of changed by heat test and unchanged sulphur corresponds with the total weight of sulphur found on the dyeing, the following table is given :—

Determination.	Total of changed and unchanged sulphur.	Total sulphur
1.	0·965	1·047
2.	0·927	1·027
3.	0·960	1·045
4.	0·970	1·020

The next experiments were carried out to determine whether a longer heating than two hours as already described would convert more of the sulphur, shown to be unchanged by this heating, into sulphuric acid, because the above tables show that the proportion of sulphur which can be converted into sulphuric acid by heating at 140° C. has a definite relation to the total amount of sulphur present. This relation is 1 of convertible sulphur to 4·5 of total sulphur present. Dyeings were heated for 14 days to 60–70° C., allowing every now and again the yarn to take up its natural moisture. Although the yarn by this treatment was completely destroyed, the total amount of sulphur converted into free sulphuric acid was not increased by this prolonged heating.

These experiments, therefore, give the definite result that heating at 140° C. for two hours is sufficient completely to convert all sulphur in the sulphur black into sulphuric acid which is convertible by this method. In other words, the sulphur that is converted into sulphuric acid and causes the tendering, is only a definite portion of the total sulphur contents of the sulphur black. Repeated experiments have been made with many sulphur black dyeings, and have confirmed the above results.

In carrying out experiments with the actual dyestuff, as distinct from the dyeings, great difficulty was found in purifying the dyestuff. The following method was carried out:—

Fifty grams of commercial black were boiled in 2 litres of distilled water. Dilute acetic acid was then added to the solution until complete precipitation of the dyestuff showed itself by spotting on filter paper. The precipitate so obtained could not be filtered, but by boiling for a quarter of an hour it gradually became thicker until washing and filtering was quite possible. The precipitate was washed until there was complete freedom from sulphate and chloride. By this method 40 per cent. pure dyestuff was obtained from the commercial dyestuff, and this had an ash content of 1·4 per cent. which consisted of alkali. The total amount of sulphur determined in this pure dyestuff amounted to 33 per cent.

For a complete conversion of convertible sulphur into sulphuric acid, the purified dyestuff was heated at 140° C., till no increase in the acid contents took place. In a series of experiments the quantity of acid formed amounted to 8·1 per cent calculated as sulphur. This gave a proportion of one part of convertible sulphur to 4·1 of complete sulphur contents, which agreed very well with the results obtained by similar treatment of the dyeings, the result in that case being 1 to 4·5.

In the experiments for the conversion of the convertible sulphur in the dyestuff into sulphuric acid it was noticed that the least traces of heavy metals played a very distinct part in the ease with which the sulphur was converted into sulphuric acid. If the dyestuff was purified so that there only remained in the ash small quantities of alkali, the sulphur colour had to be heated six times to 140° C. in order to convert the convertible sulphur completely into sulphuric acid.

On the other hand, if the least trace of heavy metals, such as iron, was present, the convertible sulphur was converted into sulphuric acid by only once heating to 140° C. The total amount of sulphur converted was the same in each case.

In order to determine the influence of salts on the formation of sulphuric acid in sulphur colours, several samples of purified dyestuff were mixed with sodium bicarbonate, sodium acetate and cream of tartar, in addition to traces of iron salts. They were heated four times for 1½ hours in damp air to 140° C. All additions accelerated the formation of acid. As is already known, acid acting salts and traces of acid were also found to accelerate the production of sulphuric acid

These results determine that the action of an aftertreatment of sodium acetate is solely effective in so far as it neutralizes any acid that is formed, but beyond this, the aftertreatment does not prevent the formation of sulphuric acid, indeed the above experiments definitely show that it accelerates the formation of sulphuric acid.

In order to prevent a subsequent conversion of the convertible sulphur on the fibre into sulphuric acid, experiments were carried out to oxidize this sulphur before dyeing. All experiments, however, showed that dyestuffs which were treated in this way lost the greatest part of their valuable dyeing properties. The more sulphur that was oxidized, the less soluble did the dyestuff become. The important fact is proved, therefore, that the convertible sulphur in sulphur black dyestuffs is absolutely necessary for the formation of a good black. The contents of convertible sulphur in the sulphur black determine the dyeing power of the black itself.

The chief results of this work may be summarized as follows :—

After removal of any free sulphur by extraction with carbon bisulphide, 20–25 per cent. of the sulphur in a sulphur dyestuff exists in the special chemically active and easily oxidized form, and is present on the fibre in the same form. Owing to its very fine state of division in the cellulose fibre it is easily oxidized and causes the tendering. The remaining 80 per cent. of the sulphur can only be oxidized to sulphuric acid by strong treatment when the colour is completely destroyed.

Sulphur, therefore, in sulphur blacks is present in three forms :—

1. Mechanically free sulphur, which may be extracted with carbon bisulphide.
2. Easily oxidizable, chemically active sulphur, which, by heating the dry dyestuff or the actual dyeing in the presence of air, is easily converted into sulphuric acid. This quantity amounts to 20–25 per cent. of the sulphur contents.
3. Firmly combined or stable sulphur, only oxidizable by strong oxidizing agents, which entails the complete destruction of the dyestuff. This quantity amounts to 50–75 per cent. of the total sulphur contents.

The mechanically mixed or free sulphur plays no part in the dyeing properties of the colour, nor does it play any part in the tendering.

APPLICATION.

The constitution of the sulphur colours is still unknown, so that no theory has been developed as to the theory of dyeing. The majority of the sulphur dyestuffs are insoluble in water and only possess affinity for the fibre when in the form of their leuco compounds. They may be brought into a perfect solution by means of sodium sulphite, but they still have no affinity for cotton. They must be reduced to the leuco compound before they possess any affinity for the fibre. This may be accomplished by alkaline reducing agents, but the one universally used is sodium sulphide, owing to its extreme suitability coupled with its cheap price. There are two qualities of sodium sulphide used in practice: sodium sulphide crystals and the quality known as concentrated or "rock" sulphide, which is double the strength of the crystals.

Storage.—Sulphur dyestuffs should be stored in a dry place and carefully covered after any colour has been drawn, as they deteriorate rapidly if allowed to become damp or exposed to the atmosphere.

Apparatus.—Brass and copper fittings must be substituted by iron or lead fittings owing to the action of the sodium sulphide on the copper.

Dissolving.—The best way to dissolve sulphur dyestuffs is to stir the dyestuff along with soda ash into a smooth paste with cold water, add the sodium sulphide, pour boiling water over the paste whilst stirring. Put under a loose steam pipe and boil 5–10 minutes. The object of stirring the colour into a paste with soda ash before adding the sulphide is as follows: should the colour have become slightly acid, the soda ash neutralizes this and does not allow the acid to act on the sulphide, whereas if the sulphide and soda ash are added together, the acid attacks the sulphide in preference to the soda ash. This means gradual deterioration of the condition of the dyebath, and I have met many instances in actual practice due to the above reason. The above method of dissolving is undoubtedly the best, but it must be admitted that in many dyehouses the dry colour, sulphide and soda ash are thrown into the dyebath dry and dissolved by boiling the bath up for ten minutes. The degree of solubility of the sulphur dyestuffs varies considerably according to their method of manufacture, because the finished product in some cases contains a little sodium sulphide, whilst others contain none. The amount of sodium sulphide required for each individual colour may be determined by experiment, but the colour manufacturer usually saves the dyer the trouble of determining it.

The sulphur yellows are easily the most insoluble of the sulphur dyestuffs: special care should be taken in dissolving them or else the true value of the colour is never obtained. It is of the highest importance to dissolve sulphur yellows in a very concentrated solution of sulphide, therefore the method recommended above should be used. It is no use throwing the dry colour into the dyebath, because proper value will not be obtained that way. The most certain way—though not absolutely necessary—to dissolve the sulphur yellows is to stir them into a paste with their own weight of caustic soda, then to add the sulphide and hot water.

Cotton.—The affinity of the leuco compound of the sulphur dyestuffs for cotton is not very great, but it is made greater by the addition of common salt or Glauber's salt, which helps to exhaust the dyebath. Common salt is most frequently used, but Glauber's salt is preferred by some dyers, particularly when dyeing fine yarns. The dyebaths are not exhausted, even when salt is added, so that baths are worked continuously in order to avoid running colour down the drain. In actual practice, therefore, the dyebaths are kept what is termed standing, *i.e.* the dye-liquor is not run off after each dyeing, but retained. Such dye-liquors require less dyestuff than a new bath, so that dyestuff is economized. There is a limit to the length of time a sulphur black dyebath should be kept standing, naturally depending on the number of dyeings put through: such a dyebath should not be kept longer than three months without letting off and cleaning out. I have met a bath which had been kept for two years without letting off, with the result that the dyeings were very dirty, due to the accumulation of dirt during that period: it must always be remembered that each dyeing of cotton leaves a certain amount of dirt behind in the bath. Since, however, the average dyehouse has not sufficient cisterns to reserve one for each colour, the usual result is that sulphur black dyebaths only are kept standing.

The method published by the author ("Dyer and Calico

Printer," 1916, p. 50) for exhausting baths of sulphur colours should therefore be borne in mind. Dyeing experiments showed that the addition of ammonium sulphate, chloride, formate, acetate, or the corresponding amount of free acid to a sulphur colour dyebath exhausted the dyebath. The following tests illustrate the method. Prepare two baths as follows :—

Bath 1.	*Bath* 2.
18 per cent. Cross Dye black BX.	12 per cent. Cross Dye black BX.
18 per cent. Sulphide conc.	12 per cent. Sulphide conc.
5 per cent. Soda Ash.	5 per cent. Soda Ash.
60 per cent. Salt.	60 per cent. Salt.

Enter the yarn into the boiling dyebath, work half an hour, add 5 per cent. ammonium sulphate to bath 2, work fifteen minutes longer. The results will be found to be equal in depth of shade, showing that bath 2 is completely exhausted.

The amount of ammonium salt or free acid added must be so regulated that the bath remains alkaline throughout.

Loose Cotton.—The dyeing of loose cotton with sulphur colours is carried out on an extensive scale owing to the ease with which shades fast to light and milling suitable for mixture with wool and shoddy for cheap suitings, etc., can be obtained. For this class of work the redder shade sulphur blacks are used, not the brighter and greener shades, which are used for fine yarns and pieces. The application is extremely simple. A boiling cistern is prepared with the requisite colour, sodium sulphide and soda ash. The bath is well raked, the cotton thrown in and boiled under. The common salt is added, and poling continued for half an hour, then the cotton is allowed to feed in the simmering bath for at least half an hour, when, unless the cistern is required, shut off steam and allow the cotton to feed in the cooling bath. In the case of blacks, the work is so arranged that two lots are worked through in the 24 hours—one lot being put in at the end of the day, and taken out first thing in the morning, another lot put in straightaway and taken out in time to get the lot in for the night. Seeing that the one done in the daytime is not so long in the dyebath as the one left overnight, some dyers, if working on a 10 per cent. standing bath, charge the bath with 11 per cent. in the morning and 9 per cent. in the evening, so as to balance the longer time in the bath of the one left overnight. A considerable economy in colour and labour will be effected if a tank fitted with an ejector is placed under the dyebath into which the colour may be run after dyeing. The first rinsing may also be run into the supply tank. If the dyebath is also provided with a valve leading into the drain, the cotton may be washed and aftertreated without removing it from the cistern in which it has been dyed, thereby saving time and labour.

The following quantities are typical of a dyebath for loose cotton :—

1st Bath.	*2nd Bath.*
15 per cent. Sulphur black.	14 per cent. Colour.
15–30 per cent. Sodium Sulphide conc.	14 per cent. Sodium Sulphide conc.
5 per cent. Soda Ash.	2 per cent. Soda Ash.
0 per cent. Common Salt.	40 per cent. Common Salt.

3rd Bath.	*Standing Bath.*
13 per cent. Colour.	12 per cent. Colour.
13 per cent. Sodium Sulphide conc.	12 per cent. Sodium Sulphide conc.
[illegible] cent. Soda Ash.	2 per cent. Soda Ash.
uch a dy nt. Common Salt.	10 per cent. Common Salt.

without letting [illegible]
which had been kept tothat 15–30 per cent. sodium sulphide
the result that the dyein It is a good practice to give the
accumulation of dirt durinde in the first bath so as to ensure
be remembered that each dyfect solution.
amount of dirt behind in thnks are first boiled out with
average dyehouse has not suffiest carried out in an ordinary
for each colour, the usual result is not available the bundles
baths only are kept standing. bags and boiled 8–10 hours

The method published by the aing is specially necessary when dyeing fine twofold weft yarn. For yarns the greener and brighter sulphur blacks are used, except in cases of backing yarns for which weight rather than beauty of shade is required. Yarn does not require so much colour as loose cotton, so that the dyebaths are charged as follows :—

1st Bath.	*2nd Bath.*
10 per cent. Sulphur Black.	9 per cent. Colour.
10 per cent. Sodium Sulphide conc.	9 per cent. Sulphide conc.
5 per cent. Soda Ash.	2 per cent. Soda Ash.
40 per cent. Salt.	30 per cent. Salt.

3rd Bath.	*Standing Bath.*
8 per cent. Colour.	7 per cent. Colour.
8 per cent. Sulphide conc.	7 per cent. Sulphide conc.
2 per cent. Soda Ash.	2 per cent. Soda Ash.
20 per cent. Salt.	10 per cent. Salt.

In the early days of sulphur colour dyeing on yarn bent sticks were used in order to prevent oxidation of the colour on the yarn. Nowadays straight sticks are practically always used. The yarn is entered into the hot bath, given two turns, steam is turned on, and the yarn worked for ¾–1 hour at the gentle boil. As previously stated, Glauber's salt is preferred to common salt by many dyers, especially for fine yarns : which to use must be decided by the individual dyer according to the class and quality of work required. For fine yarns and hosiery the best results are obtained by using no salt whatever, but a larger percentage of dyestuff is required.

Cotton Warps.—Owing to the fact that sulphur colours will withstand the crabbing, steaming, and boiling with acids to which many warps are subjected, they were immediately largely adopted for this class of work.

Before dyeing it is advisable to boil out the warps in a boiling machine as follows :—

1st Box.—Cold caustic soda liquor, 10–15° Tw.
2nd and 3rd Boxes.—Boiling water.
4th Box.—Cold running water.

In the dyeing machine the colour boxes are charged with—

2 lbs. sulphur black
2 lbs. sodium sulphide conc.
½ lb. soda ash
1½ lbs. common salt
} per 10 gallons liquor.

Subsequent dyeings require the addition of—

6 per cent. sulphur black
6 per cent. sulphide conc.
½ per cent. soda ash
2 per cent. common salt
} Calculated on the weight of warp.

In accord with the tendency of all dyeing operations to increase production and save time and labour, large warp machines containing twelve boxes are used, in which it is possible to dye warps a full black at one run.

The boxes are arranged as follows :—

Boxes 1–4 contain boiling colour.
,, 5–6 ,, running water.
,, 7–8 ,, chrome (if necessary).
,, 9–11 ,, running water.
,, 12 ,, dilute soda, soap or ammonia.

When dyeing in the long machine the colour is not all added to the dyebath at the beginning, but in the following manner : The first boxes are filled with colour solution mixed in the proportions previously given. The chrome boxes are filled with the necessary liquor, and a thread or hank is tied on to the string, which is then run through the machine. If the hank or thread is full enough the warps are tied on, and the machine is started. Running off is prevented by feeding in stock solution from an overhead tank. The stock liquor is made up as follows :—

100 lbs. black.
100 lbs. sulphide conc.
60 lbs. common salt.
25 lbs. soda ash.
100 gallons of water.

If the stock solution is made up in this way each gallon of liquor will represent about 1 lb. of colour, and thus the amount of colour added may be easily regulated. The speed of the long machine should be so arranged that any given point on the warps is in contact with the dye-liquor for 3–3½ minutes. When dyeing sulphur colours in a warp machine it is advisable to have the top rollers fixed below the level of the liquor—all fear of bronziness and unevenness is then avoided. The fittings, bearings, steam coils, etc., must all be made of iron, as copper is attacked by sodium sulphide.

Piece Goods.—Sulphur dyestuffs are successfully dyed on piece goods on an ordinary jigger, a jigger fitted with nip rollers, or on the continuous dyeing machine, though the latter is only suitable for big runs of one colour, usually black.

For piece goods the greenest and brightest sulphur blacks are used, because all sulphur blacks redden under the finishing process. The pieces are first boiled out with soda ash, to remove size, etc., and are then batched on to the roller.

The dyebath is charged with—

2 lbs. sulphur black
2 lbs. sodium sulphide conc. } per 10 gallons liquor.
½ lb. soda ash

Then—

6–8 per cent. colour
6–8 per cent. sodium sulphide conc. } Calculated on the weight of the pieces.
2 per cent. soda ash

The pieces are given 6–8 ends in the simmering bath. The dyestuff is not added all at once, but half is given at one end, then the remaining half at the second end. The addition of salt when dyeing sulphur blacks on pieces is not recommended, because it reddens the shades considerably, and there is a tendency for the selvedge to bronze when salt is present. Cotton pieces with worsted border must be dyed cold to leave the wool white, and glue added to the dyebath to preserve the wool from injury as per the following recipe :—

First Bath.	*Standing Bath.*
12 per cent. sulphur black.	8 per cent. sulphur black.
8 per cent. sodium sulphide conc.	5 per cent. sodium sulphide conc.
12 per cent. soda ash.	¾ per cent. soda ash.
¾ per cent. brown gum.	½ per cent. glue.
[illegible] per cent. Glauber's salt.	8 per cent. Glauber's salt.

The recipes given above have all related to sulphur blacks, but the sulphur blues, greens, etc., are all dyed on the same lines, though the colours, apart from blacks, are used in varying percentages according to the shade being dyed.

Machine Dyeing.—One modern tendency of the dyeing industry is the increasing adoption of machines to dye cotton in all its various stages, whilst the machines are continually being increased in size, *e.g.* machines are now obtainable which will dye one ton of raw cotton at a time. The principle of dyeing is the same, though great care must be taken to see that the colour is perfectly soluble, so that it is usual to increase the amount of sodium sulphide when dyeing in machines. Moreover, since less liquor is usually employed in machine dyeing the quantity of salt added is considerably reduced or completely omitted.

AFTERTREATMENT OF SULPHUR DYESTUFFS.

The following methods of aftertreatment are frequently used in conjunction with the sulphur dyestuffs.

Topping with Aniline Oil.—This method is confined to sulphur blacks, and is used to obtain a shade of black which is denser than the shade obtainable with sulphur blacks alone. Moreover, the blacks so obtained are faster to milling, whilst the cotton is also weighted by the process.

The following recipe will be found to give good results, though it may be varied within wide limits, thus the quantity of aniline, etc., may be increased so as to yield a darker shade.

The bath is made up as follows : 8 per cent. bichrome is dissolved in boiling water and added to the cold dyebath next 4 per cent. iron liquor, then 4 per cent. D.O.V., finally 4 per cent. aniline oil, and 4 per cent. spirits of salts, previously mixed together in a bucket, along with a little water to keep down the fumes. The bath is stirred up, and the cotton dyed with sulphur black is entered, worked half an hour cold, raised up to 195° F. (90° C.) in half an hour, lifted out, and well washed off.

Aftertreatment with Metallic Salts.—The two salts used are bichrome and copper sulphate. The former improves the fastness to milling, whilst the latter improves the fastness to light, but must not be used with sulphur black for reasons already stated. The two salts are frequently used in conjunction with each other. The method is carried out as follows :—

A fresh bath is charged with—

1–3 per cent. bichrome.	1–3 per cent. D.O.V. or
1–3 per cent. bichrome.	1–3 per cent. acetic acid or
1–3 per cent. bichrome.	1 per cent. copper sulphate. 2 per cent. acetic acid.

Work the cotton in the above for half an hour at 140° F. (60° C.).

Cotton aftertreated by any of the above methods must be thoroughly washed to remove every trace of acid. To make certain of this 1 lb. soda ash may be added to the last wash water.

Aftertreatment with Peroxide.—This method of aftertreatment is usually confined to the sulphur blues, and has the effect of considerably brightening the shades. The operation must be carried out in a wooden vessel. Ten to twenty per cent. hydrogen peroxide is required according to the depth of shade ; the bath must be made just alkaline with ammonia, excess of ammonia must be avoided or the evolution of oxygen is too rapid. Work the dyed cotton half an hour in the cold bath, then rinse and soap hot.

Sodium perborate will give the same effect.

Softening or Oiling.—After dyeing the cotton is sometimes softened with an oil emulsion, which may be made as follows; 100 lbs. palm oil are melted in an iron pan, 12 lbs. caustic soda, 90° Tw., are added, and the mixture is well stirred, covered up and left overnight, the heat being usually sufficient for saponification of the oil. When saponification is complete a sample should emulsify completely in water, without any oil separating on the surface. Ten per cent. of the above is applied to the cotton in a bath at 140° F. (60° C.), when the cotton will practically absorb all the oil, making it much softer to handle; the shade of the black is also improved thereby, due to the removal of any bronziness there may have been present.

Topping with Basics.—Sulphur dyestuffs possess a great affinity for basic dyestuffs; in fact, they may almost be said to act as a mordant for them. The resulting shades possess quite a good fastness to washing. This process is therefore frequently used for beautifying sulphur colours. Since the war this process has been the means of enabling millions of yards of navy blue to be dyed, which the trade would otherwise have been unable to dye due to lack of dyestuffs. The navy blue for munition workers' overalls has been dyed by topping a medium shade of sulphur black with methylene blue and methyl violet. The operation must be carried out carefully, because the sulphur colours have a strong affinity for basic colours, which consequently have a tendency to rush on unevenly. The dyed cotton must be thoroughly washed in order to remove the alkali and sulphide as completely as possible. Charge the cold topping bath with 5 per cent. acetic acid, work the cotton in this, then add the requisite colour and gradually raise the temperature of the bath until the colour is exhausted. The bath must be kept acid throughout the operation: this point should be watched carefully, because if the cotton has not been thoroughly washed the sulphide may otherwise act on the basic colours.

GENERAL NOTES

Sulphur dyestuffs dyed on cotton usually become brighter and richer in tone on keeping, due to oxidation by the atmosphere. Blacks, blues, and greens all become brighter on keeping. This makes matching to shade [illegible] difficult, because it is impossible to match a shade dyed, say, three months ago with sulphur colours with a dyeing straight out of the dyebath. The best means of overcoming this difficulty is to submit a small cutting of the dyed shade to hot bichrome before matching off in order to imitate as far as possible the slow oxidizing action of the atmosphere.

In dyeing with sulphur blacks a white scum often collects on the top of the liquor, and causes trouble by attaching itself to the cotton, making white marks. This white scum is due to finely divided sulphur, and its appearance may be removed by adding sodium sulphite to the dyebath which dissolves the sulphur. Any goods which show these white marks can be immediately put right by treating with hot sodium sulphite. Many people have expressed the fear that this would cause tendering. This fear is perfectly groundless, because this sulphur has no influence at all on the tendering.

One of the commonest occurring faults is bronzing of shade, particularly in sulphur blacks and blues. This may be caused in the following ways, viz.—

1. Faulty manipulation or excessive delay between lifting the material out of the dyebath and washing off, *e.g.* letting unwashed material lie during dinner hour.

2. Excess of colour on the material through having too strong a dyebath, so that the fibre becomes overloaded with colour.

3. Shortage of sodium sulphide so that the colour is not completely reduced, but only dyes on the surface of the material and therefore is quickly oxidized in contact with the atmosphere.

This bronziness is most easily removed by treating the cotton with oil emulsion as detailed under " Softening." If the use of oil is objectionable for any particular goods, then a boiling soap or strong sodium sulphide bath is the next best remedy.

A grey and lifeless shade will result, even after ample colour has been added to the dyebath, if the bath is out of condition.

Uneven shades, unless very pronounced, may be corrected by treatment with a warm sodium sulphide bath: if this is not sufficiently effective, the shade should be bleached down, because sulphur dyestuffs are very sensitive to bleaching.

Mercerized cotton on being dyed with sulphur dyestuffs loses a good deal of its lustre. A subsequent aftertreatment with a mixture of three parts good quality soap and one part olive oil emulsified with ammonia will be found to restore the lustre to some extent.

Linen, jute, hemp are dyed with sulphur colours on the same lines as cotton, though special care is required to see that the fibre is well penetrated. Artificial silk is dyed on the lines of cotton, but the temperature of the dyebath is never taken above 140° F. (60° C.), whilst less salt is required owing to the increased affinity of artificial silk for dyestuffs as compared with cotton.

In order to avoid using an excess of salt in a standing bath the liquor should be tested cold by means of a hydrometer, the bath should not register more than 8–12° Tw. Should a bath register more than this, salt should be omitted till the density of the bath has been reduced to

SECTION IX.—INDIGO AND OTHER VAT DYESTUFFS

THE vat dyestuffs from the point of view of the chemist are classified into three groups, viz. :—

Anthracene Dyestuffs.	Chloranthrene Blue.
Indigoid Dyestuffs.	Indigo, Thio-Indigo.
Sulphide Vat Dyestuffs.	Hydron Blue.

This class includes the fastest coal tar dyestuffs at present known, though it is necessary for the reader to realize that if a dyestuff belongs to the vat series it is not necessarily possessed of the same fastness as the best members of this class. There are degrees of fastness amongst the vat dyestuffs just as there are in every class of dyestuff : some vat dyestuffs are fugitive to light and poor to washing and steeping in cold water, so that preliminary tests should always be carried out before adopting them on the big scale. However, certain members are of extraordinary fastness to light, boiling soap, washing, and chlorine. Picked dyestuffs of this series are the colours which are used in the guaranteed cloths, such as casement cloth, blouse and shirt fabrics, and handkerchief cloth, which the makers sell under guarantee of replacement, if the colour fades or bleeds. Such cloths were becoming before the war quite a feature in textiles, particularly for export to countries where the sun is very powerful, so that fugitive colours are useless. The American market was taking these colours up very strongly, whilst there is no doubt that a larger trade will be built up in this class of fabric when the public have become educated to their value. Up to the present these dyestuffs have been very expensive and difficult to dye, but competition and improved manufacturing methods may be expected to gradually reduce the price and to improve their dyeing properties from the point of view of levelling and penetration.

The vat dyestuffs, with the exception of indigo and woad (long since superseded by indigo), are of very recent manufacture. The first representative indanthrene was introduced in 1901. They find most application on the vegetable fibres because their application on wool—with the exception of indigo—has hardly passed beyond the experimental stage.

On cotton it may be said in general that the anthracene vat dyestuffs are the fastest, followed by the sulphide vat dyestuffs, whilst the indigoid vat dyestuffs are the least fast. On the contrary, the indigoid class do not present the same difficulties in their application as do the anthracene class.

All the vat dyestuffs are insoluble in water, and only pass into solution when they are reduced to their leuco compounds, which are freely soluble in alkali. The material is impregnated with the alkaline solution of the leuco compound of the dyestuff, which regenerates the dyestuff on exposure to the atmosphere by oxidation, and thus precipitates it on the fibre. Dyeing with vat dyestuffs is not dyeing in the same sense as dyeing wool with acid dyestuffs is dyeing, in that there is no chemical combination of the dyestuff with the fibre, but a deposition of a pigment dyestuff in the fibre.

Indigo, which is the most important representative of the vat dyestuffs, is most probably the oldest dyestuff known to man. It has been rightly described as the king of dyestuffs and is firmly rooted in the estimation of the public as synonymous with fastness. Formerly indigo was solely obtained from the indigo plant, but synthetic indigo has been on the market since 1897, and it had practically ousted the natural product when war broke out. The manufacture of indigo synthetically has had as a natural sequence the production of the various halogenated indigos, which are now on the market.

Indigo is dyed on cotton and wool, also to a limited extent on silk: it is applied according to the same principle by which it has always been applied, *i.e.* it is reduced to form a vat in which the material is dipped and the colour regenerated by exposure to the atmosphere.

Two general methods are employed for producing an indigo vat :—

1. Reduction by fermentation.
2. Reduction by chemical reducing agents.

The first method was universally used until comparatively recently, and it is still used in the East, but its use in Europe and America has been largely discontinued in favour of the more advantageous chemical vats.

The chemical principle involved is extremely simple. Indigo (which is insoluble in water) combines on reduction with two atoms of hydrogen to form a colourless leuco compound, termed indigo white, which reacts like a weak acid, whose alkali salts are soluble in water. It is necessary, therefore, for an indigo vat to be alkaline in order to have the indigo white in solution, and capable of being absorbed by the fibre. The practical application of indigo necessitates a long experience of big-scale working in order to become efficient at it. For the details of the various vats now to be described I am largely indebted to Badische's book on indigo.

WOOL.

Indigo on wool is the standard of fastness for blues on wool. It is used in large quantities for naval and military (before the universal adoption of khaki) uniforms, but the main consumption of indigo is for the dyeing of vegetable fibres. On these fibres it is not as fast as on wool, nor is it as fast as the best of the modern vat dyestuffs.

There are only two vats which come into consideration for wool dyeing as far as Great Britain is concerned :—

1. The Woad Vat (fermentation).
2. The Hydrosulphite Vat (chemical).

In both vats the controlling factor is alkali. It of alkali is present the wool may easily be deteriorated, in addition to which excess of alkali prevents the wool from absorbing the indigo white, thus making the dyeing of dark shades difficult. A shortage of alkali reflects itself in the poor condition of the vat owing to the indigo white not being in proper solution, whilst the resulting shades both scour and rub badly owing to the indigo being absorbed too quickly and deposited on the surface of the fibre only.

In comparing the two vats it must be remembered that the fermentation vat is probably the oldest known dyeing process, whilst the hydrosulphite vat was patented in 1871 by Schutzenberger and Lalande, the British rights of which were bought by Read Holliday and Sons, Ltd. The production of sodium hydrosulphite in solid form has enabled this vat to be obtained free from sediment, so that it may be successfully used in machine dyeing. This vat has supplanted the fermentation vat in the majority of dyehouses in Great Britain, though it has not been so largely adopted on the Continent. Its great advantages are freedom from sediment, which avoids the loss of time waiting for it to settle, and thus enables the vat to be worked more frequently, so that a greater output per vat is obtained. No time is lost between setting the vat and working the same, whereas a fermentation vat cannot be worked till three days after it has been set. Again, the hydrosulphite vat (free from zinc) is the only vat in which there is no loss of indigo due to over-reduction.

Fermentation Vat.—The fermentation vat, which was most commonly used in Great Britain, was the woad vat, which requires much practical experience and a great deal of attention to keep it in good condition, and to avoid loss of indigo. Such a vat may be worked for nine months before it is necessary to exhaust it and run it off.

The following recipe is for a dark blue, though it may naturally be varied within wide limits, owing to the nature of the vat :—

Capacity of vat	2500 gallons
Indigo, 20 per cent. paste ..	60 lbs.
Woad	500 lbs.
Bran	30 lbs.
Madder	10 lbs.
Lime	12 lbs.

Heat the water up to 140° F. (60° C.), and add the crushed woad, which is stirred at intervals until thoroughly soaked or left overnight. Add the indigo, madder, bran and lime, and stir thoroughly, after which the vat is covered over to prevent loss of heat and access of air, till fermentation sets in. This will take place in 12-16 hours. When fermentation sets in the blueish-red colour will change to green, and the vat will smell sweet. The vat is well stirred and slaked lime is added in small quantities at intervals, until the liquor changes from green to yellow, with a bronzy scum, termed flurry, and the sweet smell changes to a sharp one. The vat will be ready for dyeing in two to three days from commencing to set it. When it appears to be ready, test it by dyeing a small quantity of wool in it. This should appear greenish-yellow on taking out of the vat, and will slowly turn blue on exposure to the air. On being scoured it should not lose much colour. Until the vat has become seasoned too much wool must not be worked through it. When it is in proper condition the vat is stirred up first thing in the morning, and sharpened with lime. After the sediment has settled dyeing proceeds 2-3 hours, when it is again stirred up, sharpened, allowed to settle, and dyeing continued a further 2-3 hours. Dyeing is then stopped for the day, the vat is heated up to 120° F. (50° C.). Indigo, woad and bran are added and the fermentation regulated by addition of lime and the vat covered up for the night. Next morning the vat is stirred up, lime added, if necessary, and the above procedure gone through.

The temperature of the vat should not be allowed to fall below 110° F. (45° C.), otherwise the fermentation may become too sluggish. Too active fermentation may be regulated by addition of lime, too sluggish fermentation is accelerated by addition of bran. Excess of lime produces duller shades of blue.

The soda fermentation vat is preferred to the woad vat on the Continent: treacle is used in place of woad, and soda in place of lime.

Hydrosulphite Vat.—The hydrosulphite vat was introduced by Schutzenberger and Lalande in 1871. For this process the hydrosulphite was made by the addition of zinc dust to sodium bisulphite, so that the vats gradually accumulated a sediment of zinc, which destroyed some of the indigo. The alkali first recommended was lime, followed later by caustic soda, which latter had the advantage of reducing the amount of sediment in the vat. The introduction of sodium hydrosulphite in stable powder form by the Badische company further facilitated the ease of working this class of vat, since it completely eliminated zinc from the vat, with the result that the modern hydrosulphite vat is the only vat in which no loss of indigo occurs. Ammonia has been added to the alkalies used for dissolving the indigo white, so that vats may now be obtained perfectly free from sediment, which allows the size of the vats to be reduced considerably. The hydrosulphite vat is a chemical vat in which the action of each ingredient is definitely understood, so that the vat is under closer control than is possible with a fermentation vat, nor does it require the same personal attention. The absence of sediment enables the vat to be set and used the same day, whilst all loss of time waiting for the sediment to settle is avoided, so that the possible production from the vat is much greater.

Unlike the fermentation vat, the indigo is not reduced in the actual working vat, but a concentrated stock vat is made from which definite quantities of ready reduced indigo may be measured to replenish the working vat.

Bisulphite Zinc-Lime Vat.—This vat has the largest sediment of any of the hydrosulphite vats, but nothing comparable to that of a fermentation vat. Owing to the presence of zinc in the vat, there is always a certain loss of indigo. The stock vat is prepared by mixing in a cask—

20 lbs. indigo, 20 per cent. paste.
1 gallon water.
2 gallons milk of lime, 20 per cent.

The above should be intimately mixed together—the finer the state of division of the indigo the easier is it reduced —mix in a separate vessel 2½ gallons sodium bisulphite, 57° Tw., with 2 lbs. 2 oz. zinc dust when heat is generated, and the characteristic smell of sulphur dioxide disappears: if the smell does not completely disappear then more zinc must be added till it does. This process is termed "killing" the bisulphite. When the bisulphite is killed, it is added to the indigo paste along with 12½ gallons water at 150° F. (65° C.), stirred till the paste is thoroughly mixed, covered over and allowed to stand 2 hours, or better still overnight, when it will be reduced ready for use. The working vat is heated up to 120° F. (50° C.); take out the oxygen in the water by adding ½ gallon killed bisulphite, add the requisite amount of stock vat, stir up, allow the vat to settle, then proceed to dye in the normal way.

The liquor should appear greenish-yellow: a green or blue-green colour shows the vat is short of killed bisulphite: a bright yellow colour shows the presence of too much alkali. The vat is kept in condition by the addition of killed bisulphite and lime after it has been replenished from the stock vat. The vat should not be worked longer than three weeks before it is exhausted and run off. This vat is very largely used in Great Britain.

Owing to the use of lime as the alkali the wool must finally be soured off, then thoroughly washed to prevent the wool taking up a harsh feel.

Hydrosulphite Soda Vat.—This vat is the same in principle as the bisulphite-zinc-lime vat, except that caustic soda is used as the alkali and the ready-made hydrosulphite powder is used as the reducing agent. It follows, therefore, that this vat is free from sediment, but it behoves the dyer to be very careful to avoid excess of caustic soda, which would have a very detrimental effect on the wool.

Stock Vat.—15 lbs. indigo, 20 per cent. paste, is diluted.

with 3 gallons hot water, to which is added 3 pints caustic soda, 77° Tw., and the whole thoroughly mixed, then add gradually 3 lbs. hydrosulphite powder: maintain the mixture at 140° F. (60° C.), when the indigo should be reduced in half an hour. The working vat is heated to 120° F. (50° C.), and the oxygen taken out of the water by addition of 1 quart ammonia (17 per cent.), and 5 oz. hydrosulphite powder. Add 1¼ gallons glue solution, 10 per cent., and finally the requisite quantity of the stock vat.

Hydrosulphite Ammonia Vat.—This vat is the latest vat to be introduced, and is perfectly free from sediment. Ammonia itself is almost incapable of dissolving indigo white, but it was discovered by Meister, Lucius and Bruning that indigo white was not precipitated in the presence of glue and ammonia, but assumed a colloidal form, which possesses a great affinity for the fibre. For use in this a specially reduced indigo was marketed, which consisted of indigo white plus ammonia and a minimum quantity of fixed alkali. The dyer is, therefore, saved all the trouble of reducing the indigo and simply measures a given quantity out of the cask. The commercial names of this form of indigo were indigo MLB. vat 1 and indigo solution BASF, 20 per cent.

A working vat is set as follows. For a vat of 600 gallons heat to 120° F., then add 1½–3 pints ammonia (17 per cent.), and two gallons glue solution (10 per cent.), finally 2–4 gallons of the special indigo solution and 2½–5 lbs. hydrosulphite powder. After complete stirring the vat will be clear and of a greenish-yellow colour. Wool when it is taken out of the vat should appear pale green.

This vat should not be run longer than a week. Two quarts of glue solution (10 per cent.) should be added twice during this period.

GENERAL NOTES FOR WOOL.

It is absolutely essential that the wool—in whatever form it is dyed—should be perfectly free from grease, or else bad results are sure to be obtained, particularly from the point of view of rubbing.

Carbonized wool must be thoroughly neutralized with soda before being dyed, or else the acid on the wool will completely upset the condition of the vat by neutralizing the alkali.

Before dyeing is commenced a trammel net is inserted in the vat which is arranged at such a height that it keeps the wool clear of the sediment.

The temperature of the vat should not be higher than 120° F. (50° C.), or else the alkali will commence acting on the wool.

Indigo dyeing being purely a mechanical process calls for mechanical means to be adopted in dyeing. For piece dyeing hawking machines are used, which consist essentially of two mechanically driven squeezing rollers fitted with openers so as to avoid folds of cloth passing through the rollers. The squeezing plays an important part in the penetration of thick cloths. When the cloth is taken out of the vat it is immediately passed through overhead squeezing rollers which may be run on an overhead rail from vat to vat as required. Unless the squeezing rollers are free from defect uneven pieces will result. After the pieces have been thoroughly oxidized, they must be thoroughly washed, treated with fuller's earth, then again with water. This treatment must be thorough, in order to remove all superficially attached indigo which would otherwise cause the shade to rub; if the shade has been dyed from a vat out of condition no amount of treatment will make the shade fast to rubbing.

Loose wool is usually dyed in circular cast-iron vats, which are so sunk in the ground that they project about 2½ feet above the ground. They are usually built round with bricks and fitted with a steam coil for heating purposes. When the wool is due out, a pair of squeezing rollers on wheels is brought to the side of the vat, a travelling apron is so fitted that it projects over the side of the vat, underneath which a tray is fitted so as to return all the surplus liquor to the vat. The wool is lifted on to the apron by means of sticks or forks; after passing through the nip rollers it falls on the floor where it is allowed to lie in heaps till oxidized.

Wool should be entered into the vat wet, since dry material takes in too much air which would disturb the condition of the vat.

When dyeing indigo the more dips within reason which are given the better is the wool dyed. Wool dyed to a shade in two dips will be faster than wool dyed to the same shade in one dip. The average length of dip is 20–45 minutes, but pieces which are difficult to penetrate may be kept in the vat 1–2 hours. The length of time of dip does not however, bear any definite relation to the deepening of the shade. The quick dyeing of indigo always means inferior fastness to rubbing.

It is a very common practice to bottom the wool with some red dyestuff previous to dyeing with indigo and thus economize indigo. Alizarine red on a chrome mordant is commonly used. The preliminary [illegible]roming serves the useful purpose of also cleaning the wool, thus ensuring [illegible] results.

[illegible]igo is also topped with a variety of dyestuffs to produce " woaded " [illegible] thus woaded blacks are produced by dyeing logwood on top of [illegible]ilst woaded greens are produced by combining fustic with the [illegible] When chroming on top of the indigo great care must be taken [illegible]oying the indigo, which is sensitive to oxidizing agents. [illegible] paper is a very good and easy means of testing the [illegible]t.

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Stock Vat.

COTTON.

There are three principal vats used for dyeing indigo on cotton, viz.—

1. Copperas vat.
2. Zinc-Lime vat.
3. Hydrosulphite vat.

The copperas vat is gradually falling out of use owing to the very bulky sediment produced which is five times bulkier than that of the zinc-lime vat, whilst the loss of indigo due to destruction is much greater than in the case of the other two vats. The zinc-lime vat is the one most commonly used because the causticity of the hydrosulphite vat is detrimental to the workmen's hands. The hydrosulphite vat is more advantageous in machine dyeing due to its freedom from sediment and ease of control.

Copperas Vat.—In the formation of this vat the lime acts on the ferrous sulphate to produce ferrous hydrate—

$$FeSO_4+Ca(OH)_2=Fe(OH)_2+CaSO_4$$

The ferrous hydrate is gradually oxidized to ferric hydrate (which forms the bulky sediment) and so acts as a reducing agent reducing the indigo present to indigo white, which dissolves in the excess of lime present and is thus in a condition to be absorbed by the fibre.

Stock Vat.—Thirty lbs. indigo, 20 per cent. paste, are mixed with 6 gallons of water at 140° F. (60° C.); add to this 36 lbs. quicklime made into a smooth paste, then add, whilst stirring, 24 lbs. ferrous sulphate in about 10 gallons water, and the whole made up to 60 gallons. This should be stirred occasionally, covered over, and left overnight; in the morning it should be reduced to a yellow solution with bronzy scum. Before adding to the working vat, the water should be sharpened with 3 oz. lime and 1½ oz. copperas for every 10 gallons.

Zinc-Lime Vat.—In the formation of this vat the lime and zinc dust react to form calcium zincate, whilst hydrogen is liberated which reduces the indigo to indigo white which dissolves in the excess of lime present—

$$Zn+Ca(OH)_2=CaZnO_2+H_2$$

Stock Vat.—Twenty lbs. indigo, 20 per cent. paste, and 2½ lbs. zinc dust made into a paste with 4 gallons of water at 140° F. (60° C.), are mixed together, to which is added, whilst warm, 8–10 lbs. quicklime made into a smooth paste, and the whole is made up to 20 gallons with water at 140° F. (60° C.), and well stirred at intervals. The mixture will reduce to a pure yellow. Before adding to the working vat, sharpen the water with 1 oz. zinc dust and 1½ oz. lime for every 10 gallons.

Hydrosulphite Vat.—This vat has not found as much favour as the zinc-lime vat, but the increasing adoption of dyeing machines will inevitably lead to an increasing use of this vat, due to its freedom from sediment. One objection laid against this vat is the difficulty of dyeing dark shades satisfactorily, if the vat should contain excess of caustic soda and hydrosulphite, whilst the cost of the reducing agent is also urged against it.

Stock Vat.—One hundred lbs. indigo, 20 per cent. paste, is intimately mixed with 6 gallons caustic soda, 76° Tw., and 20 gallons water, 17 lbs. hydrosulphite powder conc. is then added and the whole warmed to 110° F. (45° C.). The indigo should be reduced and ready for use. Before adding the stock vat to the working vat the water is sharpened with 1 oz. hydrosulphite for every 100 gallons water.

GENERAL NOTES FOR COTTON.

Cotton dyeing is carried out cold.

Indigo on cotton is not as fast as on wool, nor is it as fast as the new vat blues, but the latter are much more expensive to dye and do not give a good navy shade like indigo. The great advantage about indigo on cotton is that no matter how many times it is washed the shade always remains a nice blue despite loss of depth; this is not so with sulphur blues, for example, which always wash redder.

Cotton is dyed in all stages of manufacture, but very rarely in the form of loose cotton.

It is absolutely essential for the cotton to be thoroughly boiled out with alkali before it is dyed in order to get the best results.

Yarn is usually dyed by hand with a mechanical squeezing arrangement fitted over the top of the vat to ensure that all hanks are submitted to the same degree of squeezing in order to ensure all being the same shade. After this squeezing the yarn is wrung and beaten out on the peg, then hung to allow of oxidation.

A heavy shade of indigo on yarn will be passed through 6 vats, starting with a weak one and finishing in a strong vat. By this means the best results are obtained as regards to washing, rubbing, and penetration. A similar depth of shade dyed with a reduced number of dips will be proportionately less fast.

When lime is used as the alkali the yarn should be soured off with hydrochloric acid, which removes the lime in the soluble form of calcium chloride. Souring or steaming raises the bronze in indigo shades.

The dipping vat is used for heavy piece goods, whilst light goods are dyed in the continuous vat. The squeezing rollers must be efficient for level results.

Sizing of indigo yarns always dulls and darkens the shade, so that basic colours are sometimes used for topping indigo, whilst it is often combined with sulphur dyestuffs which have a great affinity for the indigo.

A novel process for the quick dyeing of indigo on cotton was described by R. B. Brown in *J.S.D.C.*, 1913, p. 71, for which it was claimed that one dip of 20–30 minutes would give a shade equal to 3–4 dips in a zinc-lime or copperas vat, whilst a heavy shade could be produced in two dips.

The process consists in setting the vat with much less caustic soda than has hitherto been considered necessary for a hydrosulphite vat, and in making an addition of common or Glauber's salt. Moreover yarn may be dyed in [illegible]o–100-lb. lots instead of the usual practice of 6 lbs. in the vat at a time. The vat is set as follows:—

For 100 lbs. yarn—

200	gallons water
44	lbs. indigo solution, 20 per cent. for cotton
4½	pints caustic soda, 42° Tw.
4½	lbs. hydrosulphite powder conc.
7	pints monopol soap
9	lbs. common or 22 lbs. Glauber's salt.

THE OTHER VAT DYESTUFFS.

It is a curious fact that although indigo was probably the first dyestuff known to man, it remained the sole representative (with the exception of woad) of vat dyestuffs until 1901, when indanthrene was put on the market. Since this date a large number of vat dyestuffs have been produced commercially, which may be divided into three distinct chemical classes, viz.—

Anthracene dyestuffs.—Algol, chloranthrene, cibanone, duranthrene, indanthrene.

Indigoid dyestuffs.—Thio-indigo, ciba, helindone, and various halogenated indigos.

Sulphide vat dyestuffs.—Hydron colours.

The above colours include the fastest colours known, and are mainly applied to the vegetable fibres. Wool cannot be dyed with the anthracene dyestuffs owing to the strongly alkaline nature of the dyebath, nor have the hydron dyestuffs been recommended for wool by their makers. The indigoid dyestuffs have been persistently recommended for wool, but so far as Great Britain is concerned, the author has not heard of them being seriously adopted. The fact of the matter is that there is a large range of fast colours for wool, which are not only cheaper, but more easily applied, whilst they also meet the fastness requirements of the various branches of wool dyeing.

Attention was called at the beginning of this section to the fact that all vat dyestuffs are not fast, but those which are fast are extremely fast to light, washing, and boiling soap. Many of these dyestuffs are fast to chlorine, so that they are used in goods which have subsequently to be bleached, but special methods have to be adopted for boiling out the goods. Although the colours are so fast very few will stand boiling in a pressure kier without marking off. In fact, it is frequently found in an open kier that the pieces at the bottom which have had the weight of the other pieces on them will have marked off, whilst those at the top have come out perfect. This is due to the fact that the alkali plus the impurities removed from the cloth form a local vat with the dyestuff and cause it to run locally. Many products have been suggested as additions to the kier to prevent marking off, but I have not heard of any being successfully adopted. The colours are, however, otherwise so valuable that the trade have reconciled themselves to the fact that it is necessary to take special precautions in the boiling-out process, and in some cases a boiling in the open jigger is all the boiling that is given. Again, many colours, whilst not bleeding, undergo a change of shade in the bleaching liquor, but the original shade may be restored by a simple after-treatment with hydrosulphite.

Of the three classes of vat dyestuffs two are much easier to dye than the third. The indigoid and sulphide vat dyestuffs are no more difficult to dye than indigo, but the anthracene dyestuffs are certainly more difficult, particularly from the point of view of penetration, though the halogenated anthracene dyestuffs, like chloranthrene blue FC, are much better in this respect than the non-halogenated dyestuffs. On the other hand, the anthracene group include the fastest dyestuffs of the three series. The sulphide vat or hydron dyestuffs were the last group to be introduced, and had really not had time to be extensively adopted before the war intervened and cut off the supply. They had been more widely adopted on the Continent, particularly for blue apron cloth. The hydron series is the only one which includes a satisfactory navy blue at a reasonable price. The other two series of colours had been gradually more and more widely adopted, though it must always be remembered that their high price limited their use to the best quality of cotton and linen goods. Their chief use has been in guaranteed casement cloths, blouse fabrics, shirtings, washing dresses, and handkerchief cloth.

The application of the vat series has been a source of great trouble to the dyer, and has presented many difficulties, but experience has been gradually gained which has enabled them to overcome the difficulties and get perfect results without the aid of such apparatus as under-water jigs, but in the ordinary Lancashire jig. The greatest difficulties are encountered in dyeing compound shades, but here again experience has enabled the dyer to choose the most suitable types. In this connection it may be said that most curious results have been obtained. Two dyestuffs which as self shades have proved themselves extremely fast, are sometimes less fast when dyed together in a compound shade. On the other hand, a colour like anthraflavone, which is not fast as a self shade, is extremely fast when dyed in combination with indanthrene blue. Experience has also shown that two dyestuffs which will not mix level in compound shades will give level shades if a small addition of a third dyestuff is made to the vat. Trouble is also caused by the fact that one dyestuff dyes best at a different temperature to the other dyestuff being used in the compound shade. In such cases dyers usually dye at an intermediate temperature. When dyeing compound shades with the vat dyestuffs it is best to reduce each dyestuff separately, and then mix them in the dye-bath in the reduced state, rather than to mix them together in the unreduced state and then reduce them. The maintenance of the correct temperature in dyeing vat dyestuffs is of the highest importance in order to get the best result obtainable from any particular type. The following experiments with chloranthrene blue BD are instructive, and illustrate the above point effectively. Dye chloranthrene blue BD under identical conditions of percentage of colour, caustic soda and hydrosulphite, but at the following different temperatures: 140° F. (60° C.), 158° F. (70° C.), 176° F. (80° C.), 194° F. (90° C.) and at boil. Sour, wash, and soap the tests together so as to give all identical treatment and compare the results when dry. This examination will show the shade dyed at 140° F. (60° C.) to be the best with a progressive deterioration of shade till at 194° F. (90° C.) the shade obtained is but half the strength and flatter than the shade dyed at the correct temperature 140° F. (60° C.).

The principle of dyeing the vat dyestuffs is exactly the same as in the case of indigo, viz. the colours are insoluble in water, but reduce to leuco compounds by taking up hydrogen, which compounds are freely soluble in alkali. The only vat used, however, is the hydrosulphite-caustic soda vat.

The anthracene series require much more alkali than the indigoid or hydron series, as will be seen from the following recipes, which give approximately the same depth of shade using 20 times liquor on the yarn.

Anthracene Series—

10 per cent. chloranthrene blue BD, 10 per cent. paste.
30 per cent. caustic soda, 76° Tw.
2½ per cent. hydrosulphite powder conc.

Indigoid Series—

2 per cent. ciba blue 2R powder.
7 per cent. caustic soda, 76° Tw.
7 per cent. hydrosulphite powder conc.

Sulphide Vat Series—

6 per cent. hydron blue G paste.
6·6 per cent. caustic soda, 76° Tw.
6 per cent. hydrosulphite powder conc.

From the above it will be seen that the anthracene series require four times as much alkali as the other two, and much less hydrosulphite. The curious thing is that a light shade requires just as much caustic soda as a heavy shade, for which I have never yet seen an adequate explanation, though as a hard practical fact it is indisputable. The caustic soda plays a most important part and requires to be calculated on the volume of liquor employed, and not on the amount of dyestuff. Without a sufficiency of caustic soda good results cannot be obtained.

The following typical recipes show the method of dyeing the three different classes.

Anthracene Class.—This class require to be dyed in a strongly alkaline bath, using 1½ gallons caustic soda, 76° Tw., per 100 gallons of dye-liquor—the same amount of alkali is taken whether a light or dark shade is being dyed.

10 per cent. chloranthrene blue BD paste.
2½ per cent. hydrosulphite powder conc.

The actual dyebath may be made up in various ways according to the material being dyed. The caustic soda and hydrosulphite may be added to the dyebath at 140° F. (60° C.), and the colour added in paste form to the bath; gently stir the bath, then wait till the colour is reduced: when, as is the case with chloranthrene yellow, the leuco compound is a distinctive colour, viz. blue, it is easy to see if the bath is reduced, but with chloranthrene blue the leuco compound is also blue. This makes it difficult till one becomes experienced to tell if the colour is reduced. Three methods may be adopted. Spotting on a white porcelain tile is one method. Dipping a piece of ground glass in the vat, then lifting out and noticing the colour of the liquor as it drops off is a second one. The third one is used by the author, and consists of drawing out some of the vat in a pipette, then allow it to dribble slowly down the side of a clean test-tube held up to the light. If the blue is reduced the liquor will be clear; but if it is not reduced, owing to the insolubility of the dyestuff in water, the undissolved particles of colour may easily be detected as the liquor runs down the side of the tube.

Another method of preparing the dyebath used in practice, particularly for piece dyeing, when the colour is added to the dyebath in two portions, is as follows. Stir the colour into a paste with two-thirds of the caustic soda and half the hydrosulphite plus a little water at 150° F. (65° C.). In the jig put the remaining third of caustic soda and half the balance of the hydrosulphite, add half the colour in the tub, give the piece one end, add the balance of the hydrosulphite and the remaining half of the colour, then another end. Dyeing is then completed in five ends, the temperature of the bath being maintained at 140° F. (60° C.). Give 3 ends in a chrome bath containing 2½ per cent. bichrome which is added at twice. Follow by 3 ends in running water. Sour with hydrochloric or sulphuric acid for three ends. Give 4 ends in a boiling soap bath charged with soap and soda ash. Finally give three ends in running water. The above illustrates one method used in practice for dyeing pieces with vat dyestuffs. The personality of the dyer, however, plays a great part in the methods employed and many variations are to be found. Some dyers used jigs fitted with nip rollers, some dispense with nip rollers. Some run the pieces straight into a chrome bath without any preliminary washing, whilst others do not use chrome. Some prepare the pieces in soap or soluble oil, others do not, yet they all get good results, which satisfy the trade. Whichever way the vat dyestuffs are applied it is a long process, because in the laboratory it takes four hours to do a comparative test of vat dyestuffs from start to finish. No scamping is permissible in the dyeing, or it will show itself in the final result, whilst only the most intelligent labourers should be employed. Pieces when dyed in the jig must run straight on the roller, or else bad selvedges will result. Again high temperatures must be avoided, because the higher the temperature the more easily does the colour oxidize and cause uneven results. To those dyestuffs which are more easily reduced and more soluble it is customary to add Glauber's salt to the dyebath in order to facilitate exhaustion.

Indigoid Class—

2 per cent. ciba blue 2R powder.
7 per cent. caustic soda, 76° Tw.
7 per cent. hydrosulphite powder conc.

Stir the colour into a smooth paste with the caustic soda and a little cold water ; hot water is then added, finally the hydrosulphite. It will usually be found necessary to boil the above to obtain perfect solution. The leuco compounds are bright golden-yellow colour, which enables the condition of the vat to be easily gauged. Greenish-looking baths are not in proper condition. Cotton is dyed at 140° F. (60° C.). The colours oxidize back slowly in the air, which makes their manipulation comparatively easy.

Wool.—The following recipe is abstracted from the maker's literature and is given as a typical recipe :—

Stock Vat—

10 lbs. thin indigo red paste are thinned with
5 gallons water, 120° F. (50° C.).
Add 3¾ gills caustic soda, 76° Tw.
2 lbs. hydrosulphite powder conc.

The whole is carefully stirred and warmed to 140° F. (60° C.) till complete reduction has taken place, then diluted to 10 gallons with water.

Working Vat of 100 Gallons.—Into 90 gallons of water at 105–120° F. (40–50° C.) are put ½–1 lb. glue (previously dissolved), and the same quantity of monopol brilliant oil. For deep shades use 3–6 oz. per gallon Glauber's salt. Add 1½–2½ oz. hydrosulphite powder conc., and ½–1 oz. caustic soda, 76° Tw. The bath is now stirred, and the required quantity of stock vat is put in and allowed to stand 1–2 hours before commencing dyeing. Upon completion of the dyeing the goods are squeezed off and allowed to oxidize, which proceeds slowly, and thus very level results are obtained. After washing the dyeings are treated in a weak boiling acid bath or slightly steamed in order to destroy the hydrosulphite.

According to Dr. Kammerer [*J.S.D.C.*, 1913, p. 68] most vat dyestuffs show no affinity for wool till 160° F. (70° C.). Monopol soap or glue, however, protect the wool from the injurious action of the alkali. If the wool is likely to be left lying about for some time it will be necessary to sour the wool (half-hour at boil with 3 per cent. sulphuric acid), in order to destroy the hydrosulphite, otherwise the colour will not be fast.

The author has confirmed this statement by exposures of helindone pink AN on flannel, one piece being boiled in sulphuric acid to destroy the hydrosulphite, one piece just washed off. The difference in fastness to light was most marked. This necessity of boiling in acid is to my mind a great drawback, because half the advantage of vat dyeing is the dyeing at low temperatures in order to preserve the condition of the wool. Moreover, the boiling with acid makes it a two-bath process, and in the case cited above made a most marked difference in the final shade.

Sulphide Vat Class—	Starting bath.	Subsequent baths.
Hydron blue, 20 per cent. paste	6–30 per cent.	4–20 per cent.
Sodium sulphide crystals ..	6–30 ,,	4–20 ,,
Caustic soda, 77° Tw. ..	3–15 ,,	2–8 ,,
Hydrosulphite powder conc. ...	2–5 ,,	1½–3 ,,

Add to the dye-liquor at 160° F. (70° C.) the dyestuff, sodium sulphide, caustic soda, finally the hydrosulphite. The vat when in proper condition is yellow. The use of sodium sulphide in conjunction with hydrosulphite has been found advantageous in that better penetration is obtained. This class of vat dyestuffs may be dyed with sodium sulphide alone, but the results are not as good as those obtained by the above method.

Whichever class of vat dyestuff is being dyed they are always soured after dyeing to neutralize the strong alkalinity of the dye-liquor, then strongly soaped, again washed, finally dried. The soaping is a most important operation, because it has a marked effect on the shade in that it both develops and brightens the shade. This adds to the troubles of the dyer, because it makes matching off all the more difficult.

SECTION. X.—THE DYEING OF UNION MATERIALS, INCLUDING GARMENTS

THE dyeing of mixed fabrics made from silk, wool, cotton, and artificial silk is a branch of dyeing which is constantly increasing both in scope and importance. This development may be put down to two causes: the constant demand for a popular article at a cheap price, due to the present tendency of the public to have cheap new clothes often, rather than expensive good clothes at longer intervals: the constant introduction of new coal tar dyestuffs with special properties for mixed fabrics dyeing with which it is possible for the dyer to obtain effects hitherto unobtainable.

There are numerous ways of making a fabric consisting of more than one fibre, and there are several ways of dyeing the same. The three main principles are—

1. The two or more fibres may be dyed separately and then woven to give shot or other effects, or the fibres may be dyed in the loose, scribbled together, then spun into yarn and woven, which is the method employed for cheap tweeds, etc.
2. One fibre—usually cotton warp—may be dyed in the warp, hank, cop or beam, then woven up with an undyed weft, which is subsequently dyed in the piece.
3. All the fibres are woven in the grey state, and subsequently dyed in the piece.

Speaking generally the fastest and brightest shades may be obtained by methods 1 and 2, but the cheapest results may be obtained by method 3, coupled with the fact that it is incomparably preferable from the merchant's point of view to hold stock in the grey, which may be dyed at short notice into any desired colour.

Modern union dyeing, as now practised, may be said to have been made possible by the introduction of the direct cotton dyestuffs which enabled fabrics of silk, wool, and cotton to be dyed a uniform shade in one bath. Before their introduction the dyeing of mixed fabrics was a long and complicated process, involving the use of many baths, coupled with great skill and experience on the part of the dyer. Single-bath union dyeing involves careful attention to the temperature of the dyebath in order to regulate the dyeing of the various fibres to the same depth of shade, but is very quick and comparatively cheap. It must not, however, be assumed that the single-bath method is without drawbacks, because it has several disadvantages. The range of shades which may be obtained by this method is a limited though gradually increasing one—bright pinks, greens and violets are still unobtainable by this method. Many classes of fabrics, such as lustre goods, cannot be dyed by this method, which is frequently termed "soft dyeing," as compared with dyeing in an acid bath for two reasons, viz.—

1. The lustre and handle of the goods is more depreciated as compared with the acid method.
2. The goods are liable to cockle and crease, whilst the dyestuffs used are not sufficiently fast to permit of subsequent crabbing in order to straighten the goods once more.

Notwithstanding these drawbacks the single-bath method is becoming of increasing importance in modern dyeing practice.

The various methods of dyeing the chief classes of union or mixed goods will now be considered in detail :—

Wool and Silk Unions.—This class of fabrics has to be dyed with a shot or solid effect.

Shot Effects are generally dyed in two baths. The wool is first dyed with colours which dye the wool, but leave the silk white or nearly so at the boil. The method of procedure is to enter the material into the boiling bath, containing Glauber's salt and acetic acid, and continue the dyeing for 1–1½ hours at the vigorous boil. The bath must be strongly acid, so that it is advisable to add some acetic acid to the dyebath from time to time to replace that which is lost by evaporation. The following colours leave the silk white or nearly so in a boiling acid bath :—

Naphthol yellow.
Tartrazine.
Xylene yellows.
Orange 2G.
Acid magenta.
Indigo extract.
Alizarine delphinol SE.
Acid reds of the XL fuchsine type.

Staining of the silk in heavy shades can hardly be avoided, so that if the silk has to be left white or dyed a delicate tint the silk must be cleared by one of the following methods :—

The silk is cleared by working in a bath of clean soft water at 100°–140° F. (40°–60° C.), alone or with the addition of a little acetate of ammonia. This treatment always removes some colour from the wool, so that it must be carried out quickly and with as small an amount of acetate of ammonia as will clear the silk sufficiently to admit of the desired shade being obtained. When dyeing the wool allowance must be made for this loss of colour.

The silk may be cleared by working in a cold to lukewarm bath containing a little hydrosulphite. This treatment also removes some of the colour from the wool.

Another method is to run the pieces in a bath of aired water containing bran about 1½ oz. to the gallon; then wash well in cold water.

The silk is usually dyed in a cold bath containing a little acetic acid with basic colours, since these give the brightest colours, therefore yield the best contrast and so enhance the shot effect.

The silk may also be filled up at low temperatures with direct cotton dyestuffs, since the affinity of these colours for silk at low temperatures is strong, whilst the average direct cotton dyestuff has no affinity for wool below 100° F. (40° C.); in fact, many will not dye the wool at still higher temperatures.

Solid Effects—The dyeing of wool and silk goods a solid shade is essentially a matter of temperature, always supposing that the colours being used are recommended as suitable for this particular purpose. The reason of this is that both acid and direct cotton dyestuffs have a strong affinity for silk at low temperatures, coupled with a poor affinity for wool; the position is exactly reversed at high temperatures in that the colour boils off the silk on to the wool. Within these two extremes there is a mean temperature at which the affinity for both fibres is alike. The mean temperature of the following acid dyestuffs shows that this varies within wide limits :—

Quinoline yellow,	140° F. (60° C.).
Orange IV,	at boil.
Fast Red,	100° F. (40° C.).

Temperature, however, is not the only determining factor, but structure of the cloth also plays a very important part in the temperature at which the dyestuff should be dyed to obtain a solid shade, *e.g.* a hard, twisted, crossbred yarn will naturally be dyed a heavier shade than a loosely spun botany yarn at the same temperature. The requisite judgment on these points can only be obtained by actual experience, and such experience is the necessary qualification of a foreman dyer.

In actual dyeing it follows, therefore, that dyeing is commenced cold, and the bath gradually raised to the correct temperature for the particular dyestuff being used. If the wool is lighter in shade than the silk the temperature of the bath must be raised to get the wool heavier, conversely if the silk is lighter the temperature must be lowered. In dyeing compound shades it is essential to choose dyestuffs which have the same temperature for giving solid shades, or else the task will be extremely difficult. Fortunately there are many direct cotton dyestuffs which dye the wool and silk a solid shade between 195–212° F. (90–100° C.), and these are excellently adapted for giving solid shades with mixtures of three dyestuffs: they are particularly suitable for production of browns, greens, olives, etc., whilst the sulphoncyanine class of dyes are excellently adapted for blue and navy shades dyed in a neutral bath.

Cotton and Silk Unions.—Temperature coupled with the correct shade of dyestuff is again the deciding factor in the dyeing of this class of fabric, which may require to be dyed in a shot or solid shade. Shot effects are obtained by first dyeing the silk with acid dyestuffs, which do not stain cotton, then filling up the cotton in a fresh bath with direct cotton dyestuffs. For this latter purpose a very careful choice of dyestuff must be made, because, as already indicated, many direct cotton dyestuffs have a pronounced affinity for silk at low temperatures. There are, however, some which have but a weak affinity for silk at low temperatures, amongst which may be mentioned direct cotton blues of the "B" and "FF" types, cotton blacks of the "BH" type, mikado and stilbene colours, benzo fast scarlets.

Filling up the cotton is carried out with the addition of Glauber's or common salt, soda ash and soap; the addition of the two latter helps to keep the colour off the silk. The temperature to which the bath is raised varies with the different dyestuffs. "BH" blacks should not be taken above 100° F. (40° C.), but "FF" sky blues may be taken much higher without staining the silk.

The principles involved in the dyeing of cotton and silk fabric solid shades are the same as those adopted in dyeing wool and cotton goods to which the reader is referred for details.

Wool and Cotton Fabrics.—The dyeing of this class of fabric is usually carried out by one of the following methods:—

(*a*) Dyeing the wool with acid colours, and then filling up the cotton in a cold alkaline bath with direct cotton colours.

(*b*) Dyeing the wool with acid colours, mordanting the cotton with tannic acid, fixing with tartar emetic, then dyeing the cotton cold with basic colours.

(*c*) Dyeing the material in a neutral Glauber's salt bath with colours which dye solid shades, or by a combination of acid colours, which dye the wool in a neutral bath, practically leaving the cotton white, and direct cotton colours which dye the cotton more than the wool.

(*d*) Dyeing the cotton in the warp with cotton colours, which are fast to cross-dyeing, then dyeing the weft in the piece with acid colours.

(*a*) This method is usually carried out with goods in which it is not of much importance that the cotton should be of exactly the same shade as the wool so long as it is covered. This is the method usually carried out in shoddy dyeing, the cotton being afterwards filled up by means of sumac and iron in the case of blacks, blues, and heavy browns, or with some suitable direct cotton colour dependent on the shade of the wool. It is also used in pile fabrics with a cotton warp back, and goods that are likely to crimp if dyed in a neutral Glauber's salt bath, such as wool and cotton unions with artificial silk effect threads. Its advantage is that one can get brighter shades on the wool by this method than by the single-bath method. For filling up the cotton a large range of direct cotton dyestuffs are available which leave the wool unstained at low temperatures whilst having a strong affinity for cotton. This dyeing of the cotton should not be carried out absolutely cold, because experiment has shown that the temperature at which it is carried out has a very distinct influence on the fastness to rubbing on the cotton. The higher the temperature at which the filling up of the cotton is carried out, the faster to rubbing is the cotton; thus, if the filling up is carried out cold, the cotton will be liable to rub, but if carried out at 120–140° F. (50–60° C.), the cotton will be found quite fast to rubbing; moreover, the higher the temperature employed, the better the value obtained from the dyestuff. This operation is usually carried out on the washing machine, which enables a very short liquor to be used, and in which the heavy roller plays an efficient part in squeezing the colour into the centre of the material.

As assistants take 1 lb. Glauber's or common salt and 2 ozs. soda ash per 10 gallons liquor. This is a great advantage over the old method of sumac and iron with subsequent shading with basic colours, because the shade of the wool was always flattened, whilst the basic colours also rubbed.

(*b*) The wool is dyed in the usual manner with acid colours, washed well, mordanted with tannic acid, fixed with tartar emetic, then dyed with basic colours.

This process is very long, and requires no less than four distinct baths, and at least four washings. Despite this drawback its use is indispensable for solid shades in bright pinks, greens, blues, and violets. It is also the method usually employed for the production of shot effects.

Single Bath or Neutral Bath Method.—Owing to the many improvements in the colours suitable for this process the adoption of this method has recently largely increased. Though it is still impossible to obtain certain bright shades such as vivid greens, pinks, and violets by this method, a constantly increasing range of shades may be obtained, notably blacks, blues, browns, khakis, greens, reds. The principles involved are as follows: for the purposes of single-bath union dyeing dyestuffs may be classified as follows:—

1. Acid dyestuffs which possess a good affinity for wool (and silk) in a neutral bath, so that they may be used for shading the wool in union dyeing. A very large number of acid dyestuffs have practically no affinity for wool in a neutral bath, and are therefore useless for this purpose. A fair number are, however, suitable, amongst which may be mentioned—

Acid violets.	Fast Red.
Indian yellow.	Orange II. IV.
Rhodamine B, G.	Sulphoncyanine.
Acid blacks.	Gloria blacks.

2. Direct cotton dyestuffs which in a neutral bath give practically a solid shade on wool, silk, and cotton fabrics.

3. Direct cotton dyestuffs, which in a neutral bath dye the cotton much heavier than the wool.

By using combinations of the above three classes solid shades may be easily obtained after a little practice. One or two examples will suffice to illustrate the method. There is no direct cotton navy which will give a solid shade on wool, silk, and cotton, therefore one must build one up or buy it ready mixed by the colour manufacturer. Direct black BH dyes the cotton a full navy, whilst only staining the wool and silk a dirty grey. A navy blue is wanted which will dye the wool and silk in a neutral bath; the sulphon-cyanine class of blue does this, so the requisite percentage is found out by dye-test. Should the shade be a little flat on the wool, then some acid violet is added to brighten the shade.

Again, there is no direct cotton violet which will give a solid shade on wool, silk, and cotton. All dye the wool redder than the cotton. This redness of the wool and silk may be corrected by using a blue shade acid violet, which will dye the wool and silk only.

The successful application of this method depends largely on the intelligent appreciation of the two following cardinal points:—

(1) Use as concentrated a dye-liquor as possible.
(2) Careful regulation of temperature.

(1) The usual amount of liquor employed is 200 gallons of water for 100 lbs. material; if more liquor is taken then, proportionately more colour will be required.

(2) The temperature requires to be carefully regulated, owing to the fact that cotton has the greater affinity for the colour below the boil, whilst the wool has the greater affinity at the boil. It is therefore possible, by regulating the temperature, to control the shades of the wool and cotton within certain limits. If the wool is not heavy enough, work at the boil for a short time; on the other hand, if the cotton is not heavy enough, shut off steam and allow the cotton to feed in the cooling bath. When the difference in the shade is too great to be corrected in this simple way,

recourse is had to shading with suitable colours. If the wool has to be corrected, add an acid colour which possesses a good affinity for wool in a neutral bath, and work at the spring boil; if the cotton has to be corrected, shut off steam and add a direct cotton colour which has a much greater affinity for cotton than wool, and work in the cooling bath. It is absolutely essential in this class of work that the cotton be slightly heavier than the wool, so that the cotton does not stand out prominently ("stare" is the term often used) when the shade is examined. There are two methods of working employed in practice :—

(i) Enter cold, raise to boil in half an hour, dye at the simmer for half an hour, shut off steam and allow to feed in the cooling bath half an hour.

(ii) Enter at the boil, work 20–30 minutes at the gentle boil, shut off steam and work half an hour in the cooling bath.

Both the above methods are used, but the author prefers the former owing to the fact that the cotton gets well covered before the wool begins to take up the colour. No hard-and-fast rule can be laid down as to the length of time to keep the bath simmering. This must be left to the judgment of the individual dyer, since so much depends upon the nature of the wool, also the twist of the yarn, the weave and design of the material. In general practice, however, it may be laid down that vigorous boiling is rarely required, because the wool will usually take the colour to the desired extent at the spring boil. An exception must be made in the case of pale shades, when it will be necessary to vigorously boil the material in order to get the colour on to the wool, because many colours which yield a solid shade in a full percentage without being boiled, require to be boiled when dyed in a small percentage in order to get the colour on to the wool. Even with vigorous boiling it will sometimes be found necessary to add an acid colour with a good affinity for wool in a neutral bath in order to bring the wool to the shade of the cotton. Except in pale shades the baths are not exhausted and may be kept for subsequent lots.

The following varieties of union material require to be specially mentioned :—

Union Felt.—This material must be dyed as quickly as possible, because it is very liable to stretch in the hot liquor. The winch must also be fixed as near the surface of the liquor as possible so as to reduce the drag on the cloth to a minimum.

Mohair Pile Fabrics.—If the goods have been curled it is not advisable to employ the single-bath method, because in the hot neutral liquor the curled portions become straight again. This curled class of goods are, therefore, usually dyed with acid colours, the cotton, jute, or linen warp either being dyed with colours fast to acid cross dyeing or else they are suitably backed when made up into rugs, mats, tablecloths, etc. If the pile is not curled, then the goods may be dyed in a single bath; since the warp does not show it is only essential that it is dyed darker than the wool, but it need not be exactly the same tone as the wool. Glauber's salt should be reduced to a minimum, and when washing off sour with a little acetic acid.

Union Hose is probably the most difficult of all half-wool material to dye, because, when stretched as in actual wear, the slightest difference in tone between the wool and cotton at once becomes very noticeable. The matching of the shade on the wool and cotton requires to be very accurate. Moreover, a combination of colours which will give a solid shade on one quality of union hose will not give the same result on a different pattern. Great experience is therefore required by the dyer of this class of material.

Shades of Union Goods fast to Milling and Washing.—The after-treatment of direct cotton dyestuffs with formaldehyde and bichrome as described in Section V., is destined to become of great importance in the dyeing of fast to milling and washing shades on union goods. The introduction of dyestuffs suitable for formaldehyde aftertreatment was one of the features of the dyestuff market prior to the war, and no doubt it will be fully developed when circumstances once more permit. Fast washing blacks have been largely dyed by this process on union waste and angola yarns for a number of years and navies to a lesser extent.

Similar fast shades in olives, greens, browns and drabs may be dyed by using colours which are suitable for after-treatment with chromium fluoride as detailed in Section V.

SHODDY DYEING.

The dyeing of pieces containing a cotton warp with shoddy weft is usually carried out in one of the three following ways:—

(1) Stripping and dyeing in the same bath.

(2) Dyeing the weft with acid colours, then filling up the cotton on the washing machine with direct cotton colours or with sumac and iron.

(3) Single-bath method of union dyeing in a neutral Glauber's salt bath.

Stripping.—In many cases it is found necessary previous to dyeing to strip the dark-coloured shoddy in order to obtain a suitable ground for the desired shade. The method of stripping is carried out in various ways, amongst those usually employed the following may be mentioned:—

(*a*) Work for half an hour at 100–140° F. (40–60° C.) with 5–10 per cent. soda ash, then wash well.

(*b*) Boiling with 5–15 per cent. sulphuric acid for half an hour; this is frequently effective in cleaning the piece, especially if the shoddy was originally dyed with wood colours. Previous to dyeing, the pieces should be well washed to remove excess of acid. If they are subsequently to be dyed by the one-bath method, they must be effectively neutralized with soda ash in order to prevent the colour striking on to the wool and therefore leaving the cotton uncovered.

(*c*) Boiling with 3–8 per cent. sodium bichromate and 6–12 per cent. sulphuric acid; this is perhaps the method mostly employed, and gives very good results, stripping the goods to a medium brown bottom. This can be made lighter by a subsequent slight stripping with hydrosulphite.

(*d*) Hydrosulphite is now frequently used for stripping purposes and is very effective in all cases except where the shoddy was originally dyed with indigo; in this case the goods will look stripped in the bath owing to the hydrosulphite reducing the indigo, but on washing off the pieces the indigo oxidizes up again. In cases where indigo is present the bichrome and acid is the most effective method. As mentioned above, hydrosulphite is frequently used after stripping with bichrome to make the bottom still lighter. In all cases the stripping is carried out at 120–140° F. (50–60° C.), which gives a better handle to the goods than if they are stripped at the boil, though this temperature may be employed if the shoddy is difficult to strip. After stripping and washing, the pieces must be soured with D.O.V., otherwise the pieces are very liable to come out flecky. Hydrosulphite may be made for this purpose by the dyer himself. For this purpose bisulphite of soda and zinc powder are required. Hydrosulphite being made by stirring 13 ozs. zinc into every gallon of bisulphite used. The liquid heats up as the zinc is stirred in, and stirring is continued till the original smell of the bisulphite has disappeared, when the bisulphite is said to be "killed." It is allowed to settle and the clear liquid drawn off and used. No more hydrosulphite should be made than is required for immediate use, because it decomposes on standing. Hydrosulphite in a solid and stable form is now on the market and has largely supplanted the use of bisulphite and zinc owing to its greater convenience, though the author thinks the freshly prepared hydrosulphite is the more effective.

Dyeing.—1. In this process the goods are first boiled with the bichrome and sulphuric acid for quarter of an hour, steam is shut off, and an acid colour is salted in, steam put on again, and the piece dyed to shade. The shades that are usually obtained by this method are olives, browns, and drabs, which are somewhat near the brown bottom obtained by stripping alone, *i.e.* to say where only a small quantity of colour to change the bottom to the desired shade is required. The cotton is treated with a small quantity of sumac, then with iron liquor, and finally shaded with bismarck brown, chrysoidine, and auramine, or it may be filled up with the direct cotton colours. This is done cold with the addition of Glauber's or common salt and soda ash, using 1 lb. salt and 2–4 oz. soda ash per 10 gallons liquor. The amount of liquor employed should be as small as possible, and as the baths are not exhausted, the liquors may be kept for subsequent pieces. The filling up of the cotton should be carried out on the washing machine because the constant squeezing through the heavy rollers ensures the piece being penetrated. It may here be noted that pieces in which the cotton is filled up with direct cotton colours do not rub like those in which the cotton is shaded with basic colours, added to which the colour of the wool is not altered to the same extent as when the cotton is filled up with sumac and iron, the latter, however, adds weight to the pieces.

The necessity of shading the cotton to the exact shade of the wool depends largely on the weave of the piece. If the cotton warp is well covered, so long as the cotton is stained the shade is not of much importance; in cases where the cotton shows on the surface of the cloth it is necessary to match the shade of the wool exactly or else the cloth will have a mottled appearance.

2. In this method the weft is dyed with acid colours and the cotton is subsequently filled up in the manner described in the previous method.

3. This method of dyeing in one bath with the addition of Glauber's salt and soda ash, it should be remembered, has its limitations, but whenever it can be employed it will be

found considerably cheaper owing to the less time required, thus saving labour and increasing the turnout. The colours which are successfully dyed on the large scale by this method are blacks, browns, drabs, and fawns (gaiter cloth shades), scarlets, reds, bordeaux, and some shades of navy blue and green. When using the one-bath process the necessity of thoroughly neutralizing the cloth if it has been stripped cannot be too strongly emphasized, because if the cloth contains any acid, then the colours strike rapidly on the wool, leaving the cotton bare. The following points should also be borne in mind: The less liquor employed the less colour is required, and *vice versâ*, because, except in light shades, the dyebath is never exhausted. For the same reason steam-coils are better than steam-pipes. The cotton takes the dye better below boil, whilst the wool covers better at the boil; when boiling, therefore, the baths should not be vigorously boiled, but should be kept at the spring boil. The dyer is thus able to control the shade within certain limits by regulating the steam. If the wool is heavy enough but the cotton thin, shut off the steam and allow the cotton to feed in the cooling bath. If the bath is on the alkaline side, it favours the better covering of the cotton. In fact, if the pieces have been stripped and neutralized, it is advisable to add 1–2 per cent. soda ash to the dyebath to ensure that the bath does not become acid owing to the goods being imperfectly neutralized, whilst it also counteracts the property of shoddy that it more readily takes up colour than wool which has not been previously dyed.

Mixture effects are obtained by leaving the shoddy its original colour and staining the cotton on the washing machine in a cold alkaline liquor with some suitable direct cotton dyestuff.

Garment Dyeing.—Modern garment dyeing may be said to have been made possible by the introduction of the acid and more particularly direct cotton dyestuffs, because it is with these two classes that the satisfactory results now obtained are produced. Prior to the introduction of union blacks garments were dyed with logwood black, and the full process took five days, whereas it is now possible for a garment to be dyed black and returned within twenty-four hours, by use of union blacks. Garment dyers are unique in the variety of fabrics which they handle, making a complete knowledge of all classes of dyestuffs, coupled with a wide knowledge of fabrics, essential to success. No two garments received are alike in their structure or history. They may consist of silk, wool, cotton, and artificial silk, all on the one garment. To add to the difficulty the natural silk may be weighted and the artificial silk may be of two varieties which reflect themselves in the different way they take the dye. Moreover, the garments are frequently dirty, faded, and in many cases tender, so that it is impossible to dye them without damage or shrinking. It will thus be seen that though a garment dyer is often rather contemptuously referred to as a "job dyer," garment dyeing is in reality a most difficult section of dyeing.

In the main the garment dyer employs two methods of dyeing, viz.—

1. Dyeing the wool and silk in an acid bath with acid dyestuffs and filling up the cotton in a subsequent bath with direct cotton dyestuffs.
2. Dyeing in a neutral bath with a combination of dyestuffs suitably chosen to give a solid shade.

Both methods have their advantages, the second process being the quicker and is practically always used for blacks, which is the chief colour dyed in the garment trade. This method is often termed "soft dyeing," as contrasted with the acid method. The first method is commonly used for goods which are badly faded, as this method gives the best result on faded goods and enables brighter shades to be dyed on bad grounds than is possible by the second method. Black is naturally the most important colour for a garment dyer, and is usually dyed by the single-bath method. For this purpose union blacks ready mixed by the colour manufacturer are used, and they are dyed with the addition of Glauber's or common salt. As assistant in the dyebath many dyers prefer to use common salt to Glauber's salt, as they claim the former does not soften the goods like the latter. This has been shown by experiment to be due to the fact that a solution of Glauber's salt becomes alkaline whilst hot, but becomes neutral again on cooling, whilst a hot solution of common salt remains neutral. It is the alkaline condition of Glauber's salt whilst hot which produces this softening of garments which has been noticed by practical garment dyers.

When dyeing garments by the neutral-bath process care should be taken that the garments are not acid, which would cause the colour to rush on to the wool to the detriment of the cotton. We have met several garments which have been in an acid condition, especially in dress goods. The reason is because experience has shown that if the wool is left slightly acid after dyeing, the colour is less likely to rub than when neutral or alkaline. Dyers of dress goods, therefore, often send out their goods slightly acid. The desirable properties for a union black to have are as follows:—

1. It should work for months in a standing bath without deterioration of shade.
2. It should not bronze.
3. Its shade should be bloomy, so that it gives a good black on bad bottoms.
4. It should possess great covering power.
5. It should be non-alkaline, so that it does not soften the garments.

In practice it is dyed by two methods, either of which gives good results, so that the choice of method must be left to the individual dyer.

1. Dye three-quarters of an hour at 195° F. (90° C.) with the addition of 10 per cent. salt.
2. Enter at the boil, dye 20 minutes at the boil, shut off steam and dye 30-40 minutes in the cooling bath, 10 per cent. salt being used as assistant.

The general methods employed have already been detailed earlier in this section, so that they need not be repeated.

Dry Dyeing.—This is the erroneous term given to the dyeing of garments in a benzine and methylated spirits bath. It is employed for dyeing delicate made-up silks, etc., which cannot be unpicked, but which would be damaged if dyed in water. It is a difficult process to carry out, but has been much improved of recent years. Farrell published an interesting paper in *J.S.D.C.*, May, 1908, to which the reader is referred for full details.

The following is one method used on the big scale. First, make a benzine soap as follows: 4 gallons oleic acid are saponified with ¾ gallon ammonia (22 per cent.), finally add 20 gallons benzine. Make ½ per cent. solution of the colour in methylated spirits, and allow the salt, etc., in the colour to settle, then pour off the clear solution—all the colours do not dissolve perfectly clear, but go clear when added to the benzine soap—and this solution of colour will mix in any proportion with the above benzine soap. The depth of shade obtained depends upon the strength of the solution and length of time of dyeing; after dyeing, the shades may be washed in benzine without loss of colour.

All the basic dyestuffs are soluble in methylated spirits, but preference should be given to those acid and other colours which are sufficiently soluble in methylated spirits for this purpose. Several colours of the sulphonated triphenylmethane class are suitable for this purpose, such as acid violets, acid greens, patent blues, etc., whilst spirit induline and nigrosine are also used.

Tin-weighted Silk.—This material is a constant trouble to garment dyers, because it so frequently tumbles to pieces when being re-dyed. This is only to be expected, since the so-called silk contains at least as much tin compounds as natural silk. A simple test to distinguish between unweighted and tin-weighted silk is to boil some with a little alizarine orange paste. If the silk is tin-weighted, the silk will be coloured bright orange, owing to the combination of the alizarine orange with the tin on the fibre; a pure silk will only be stained a dull bluish pink. If the silk is highly coloured the colour should be first stripped before the test; since tin-weighted silk is dyed mostly with basic colours, repeated extractions with methylated spirits will often have the desired result.

Another test is to boil the silk with logwood and acetic acid, when tin-weighted silk is coloured violet due to the formation of the tin lake, whilst unweighted silk is stained the colour of the logwood solution.

The Dyeing of Faded Garments.—The term "faded garment" has a double meaning to the garment dyer. A garment may have been dyed with a fugitive colour, which has faded so quickly that the atmospheric influences have not had time to attack the fibre. Such a garment presents no difficulties for the intelligent garment dyer, because he is able to strip the colour and make a satisfactory job of the garment.

Another garment may be dyed with fast colours, but the fibre itself may have been badly "burnt" by the sun and atmosphere combined, especially about the shoulders; covert coatings are a good example In many cases it is impossible to dye such a garment any colour but black, which is the garment dyer's salvation, because fades usually cover up in black, and do not show like they do in green, navy blue, and brown.

The following notes deal in detail with the comparative behaviour of the different classes of dyestuffs to faded and non-faded wool.

Basic Dyes.—Typical basic colours, viz. chrysoidine, magenta crystals, methyl violet, and malachite green, have a very much increased affinity for those portions of the wool which have been exposed.

The basic colours all dye the faded portion a heavier shade, but no such definite rule can be laid down for the other classes of colours.

Direct Cotton Dyes.—These are, of course, of great importance in the garment trade, as the basis of all union dyeing and for the purposes of filling up the cotton linings and stitchings in garments of which the wool and silk have been dyed with acid colours. These colours obey no hard-and-fast rule. Chrysophenine dyes the faded flannel lighter, but chlorazol red A dyes both faded and unfaded flannel a practically uniform shade, allowing for the fact that the faded portion must from its very nature be expected to dye flatter, since all the dirt is not removed from it. Chlorazol deep brown B and chlorazol green G both dye the faded flannel very much heavier. Brown and green are the two shades which, apart from navies, show up the fades worst in actual garment-dyeing practice.

The comparative affinity for the faded wool depends a great deal on the percentage of dye used. Thus chlorazol red A dyes much lighter on the faded wool in a light shade, whereas in a full shade it is level. Chlorazol deep brown B and chlorazol green G also behave differently according to the depth of shade.

Direct cotton colours dyed at 110° F. (45° C.) show that the same thing which happens at the boil takes place at lower temperatures, such as are used for filling up the cotton linings and stitchings. This property is often very annoying to the garment dyer, because he may have got a perfect job in dyeing the wool and silk, but may find on taking the garment out of the cotton filling-up bath that the colour has flushed on to the faded portions, and so spoilt the job.

Mordant Dyes.—These dye on fades, though they are not practical politics in the garment-dyeing trade. Usually the chrome-mordant method gives a more favourable result than the single-bath method from the point of view of levelling. This confirms the ordinary loose wool-dyeing experience, viz. that chrome mordant always gives the most level results on badly mixed wools. Alizadine yellow BN gives favourable results; alizadine orange M gives passable but less favourable results. Alizadine brown M gives a very bad result by the single-bath process, whilst the result on chrome mordant is in contrast very good. This result with alizadine brown M is unexpected, because in ordinary wool-dyeing it gives very level results even on mixed wools. When the same three colours are dyed by the top-chroming process, alizadine brown M dyes the fades much heavier, whilst alizadine yellow BN and alizadine orange M give quite good results.

Alizadine red WB on a chrome mordant dyes the fades much heavier than the non-faded wool, whilst alizarin cyanine ND extra gives very level results, especially for a navy.

Here again no hard-and-fast rule may be laid down but each individual colour has to be tested to see how it behaves on faded wool.

Acid Dyes.—These are of paramount importance in the garment trade. It may be said at the outset that no hard-and-fast rule can be laid down for their behaviour towards faded wool, some are very bad and some are very good. Experience has gradually taught the garment trade which colours give them good results, and it is with the help of this class of colour that the best results are obtained on faded garments.

Some acid colours are utterly unsuitable for faded work. Fast acid red RH dyes the faded portion a much flatter and yellower shade than the unfaded portion. Fast acid blue RH goes much heavier on the faded portion. XL brown RH is an extreme example of an unsuitable colour, the faded portion being dyed very much heavier than the unfaded portion.

Three colours which are great favourites with garment dyers, owing to them covering the fades equally as well as the non-faded portion, are indigo extract, XL fuchsine 6B, and acid magenta. In these cases there is no line of demarcation visible between the faded and unfaded portion, thus proving their suitability. Many other acid dyes are equally suitable.

Colours in which my results on this artificially exposed flannel differ absolutely from garment-dyeing practice are those belonging to the sulphoncyanine class. Garment dyers vary in their attitude to these dyestuffs, but some condemn them, because they say it rushes on to the fades and dyes them much darker. My tests always show the reverse (and I have repeated the tests again and again), the faded portion always being lighter whether dyed neutral or acid; acid even accentuates the effect.

In testing acid colours on fades one can get a variety of results with one and the same colour, according to the acidity of the dyebath.

Again, acid colours which dye level on fades in an acid bath do not dye level in a neutral bath. This, of course, confirms garment-dyeing experience, viz. that the acid bath is the best medium for covering up the fades, and is always to be preferred to a neutral bath for faded work. The union colour dyeing all fibres in one bath is in theory the garment colour par excellence, but in practice its behaviour on fades prevents its universal use.

It is also unfortunate for the garment dyer that a strongly acid bath should cover the fades better than a weakly acid bath, because he naturally wishes to keep the acid down to a minimum to prevent tendering of the cotton stitches and linings. Hard boiling also favours the covering of fades, but this again is detrimental to the garments by stretching them out of shape, and also by forming steam pockets which burst the seams.

Vat Dyes.—The results of indigo and sulphide blacks dyed in the hydrosulphite vat are most striking in that indigo practically does not dye faded flannel at all, whilst sulphur blacks dye the faded flannel heavier than the non-faded. These absolutely contradictory results show how difficult it is to build any theories on exactly what happens to the wool fibre on exposure to the atmosphere.

It is an interesting speculation as to what happens to the wool fibre during the exposure. If the exposure is at all prolonged, the surface fibre becomes very brittle, and by brushing the flannel with a strong brush all the surface fibres may be brushed away, leaving the wool very bare. The same thing happens in a dyed faded garment; if you scrape the surface with a knife the wool underneath is found to be dyed the normal shade.

I have come to the conclusion that there is a partial destruction of the amido groups. If exposed flannel is diazotized and then coupled with α-naphthylamine, the faded portion is much less strongly coloured, which points to the destruction of amido groups.

Now, what is the remedy for this faded trouble, *i.e.* a remedy which may be applied in actual practice to garments, many of which are received in a tender condition?

Every conceivable remedy I could think of has been tried, but without meeting with any success. The best result obtained was by chlorinating the flannel previous to dyeing. It is, however, not to be recommended for treating faded garments in practice, as the fibre is very much affected. It makes the faded portion slimy and excessively tender, which, of course, must be avoided at all costs.

Patterns submitted to a reduction treatment (boiled with sodium sulphite), superficially seemed to have given a good result, but the faded portion was very harsh to handle and felt bare, and closer investigation showed that the result was simply due to the alkalinity of the sulphite baths, which removed the surface fibres from the faded portion. Treatment with weak alkali produced exactly the same result.

Bleaching with sodium bisulphite produces no improvement, nor does stripping with sodium hydrosulphite.

The experience of the garment trade has shown an oxidation treatment to be the best remedy for cutting up the fades. My experience on the artificially faded flannel does not confirm this, showing how difficult it is to get on common ground in this subject.

Patterns bleached with hydrogen peroxide show that this treatment makes the fade resist the colour. Permanganate has no effect, whilst stripping with bichrome and sulphuric acid accentuates the difficulty by making the contrast between the faded and unfaded portions greater.

Nitric acid cuts up the fades very well, but it also unfortunately tenders the cotton stitchings and linings, so that it is not practicable to use it for garment work. It occurs over and over again in faded work, that the best agents for correcting (or cutting up, as it is termed) the fades cannot be used on garments because the process would tender the garments.

The garment dyer alleviates the problem by choosing the dyestuff which experience has shown to give the best results in practice. If the job comes out too bad to return, the dyer suggests that it should be dyed black, which usually covers up the fades, because, as already stated, black does not often show up the difference between the faded and non-faded portions.

The Lodge-Evans Process.—The author has already given reasons in Section VIII. why he does not consider this process of practical importance for the dyeing of wool, but he does consider that it will be of great utility in certain processes of union dyeing, so he has reserved the full discussion of this process for this section. The Lodge-Evans process is so called after its co-patentees, Messrs. Lodge and Evans, of Huddersfield, who took out two patents in 1914. The process depends on the fact that sodium sulphite will dissolve sulphide dyestuffs to a perfect solution, yet this solution has no dyeing power. If ammonium sulphide or sodium hydrosulphite is now added to this solution the dyestuff reduces to its leuco compound, and will now dye silk, wool, and cotton at suitable temperatures. The question at once arises, why not leave out the sodium sulphite, since the sulphur dyestuffs may be reduced with the ammonium sulphide or sodium hydrosulphite alone? This is quite correct, but the baths do not keep in condition so well nor are they as easy to work. Sodium sulphite has a very favourable influence on the condition of the bath, making them very much easier to work.

The Lodge-Evans process is, therefore, a vat dyeing process, and it requires the same precautions to be taken. The colour must be perfectly reduced or else shades will be obtained which will rub badly, and the requisite mechanical precautions must be observed in seeing that the goods are evenly squeezed and are not allowed to lie about with a surplus of liquor in them.

As has been previously stated, the dyeing of unions is a matter of temperature, and it applies equally to this process. If dyeing is carried out cold the cotton only is dyed, whilst the wool and silk are only stained; if the temperature of the bath is raised the wool and silk become more and more dyed until a temperature is reached at which a solid shade is obtained. This temperature varies with the different colours. Sulphur blacks give solid shades about 150° F. (65° C.). Sulphur blues, greens, browns, and yellows give solid shades about 100° F. (40° C.). It is the author's experience that the wool is more or less tendered when dyeing solid shades whether it is dyed by the ammonium sulphide or hydrosulphite reduction, and is therefore of opinion that it will not be largely used for solid shades. However, if dyeing is carried out cold the wool is not tendered and the cotton only is dyed. It is this particular application which will be most useful because it opens great possibilities. It makes possible the dyeing of cotton warps already woven into pieces in fast shades which will withstand cross-dyeing the weft in an acid bath. This enables solid or shot effects to be obtained at will. It also enables union pieces to be woven in the grey and the warp to be subsequently dyed a large range of fast colours instead of dyeing in the warp form and weaving the coloured warp. It also enables the cotton to be filled up subsequently to dyeing the wool with faster shades than it is possible to get with the average direct cotton dyestuffs used for this purpose. The only defect of this process is due to the fact that all sulphur yellows possess such poor fastness to light compared with the other members of the sulphur group.

The following is the method of carrying out the two reductions :—

Ammonium Sulphide.—Boil the colour with twice its weight of sodium sulphite cryst., then add its own weight of sodium sulphide conc., and boil till the colour is in perfect solution. Cool down the bath and add double the weight of ammonium sulphate as sodium sulphide conc., when ammonium sulphide and sodium sulphate are produced in the bath by double decomposition. Ammonium sulphide has not the same tendering action on wool that sodium sulphide has.

Hydrosulphite.—Boil the colour with four times its weight of sodium sulphite cryst. till the colour is in perfect solution, allow the liquor to cool, then add equal weight of hydrosulphite powder conc. to that of dyestuff, when the colour will be completely reduced.

It is necessary when boiling the colour with sodium sulphite to use only a small quantity of water in order to get the colour into solution. Formaldehyde compounds of hydrosulphite must not be used because formaldehyde acts on the colour and destroys its affinity for the dyestuff, whilst caustic alkali is also split off into the bath. The hydrosulphite method yields a much cleaner bath than the ammonium sulphide one, whilst the smell of ammonium sulphide is decidedly unpleasant. When dyeing sulphur yellows by the hydrosulphite process it is necessary to add a little caustic alkali to the bath to ensure perfect reduction of the dyebath. On artificial silk ammonium sulphide gives much fuller shades cold than with hydrosulphite, but the latter preserves the lustre much better. The hydrosulphite process deserves serious consideration for the dyeing of sulphur dyestuffs on artificial silk, because the bath may be worked cold and the lustre is much better preserved than when either sodium or ammonium sulphide is used.

On cotton and artificial silk mixed goods this process gives excellent results from a cold bath. Direct cotton dyestuffs are used as a rule for this purpose, but it is well known that it is very difficult to dye solid shades on the cotton and artificial silk due to the much greater affinity of the artificial silk for the dyestuff. This difficulty is nothing like so pronounced with sulphur dyestuffs dyed by this process. Goods after being dyed by this process should be washed off, soured, then again washed before drying.

SECTION XI.—COLOURS PRODUCED ON THE FIBRE BY THE OXIDATION OF COAL TAR PRODUCTS

THE colours described in this section are not dyestuffs in the same sense as those described in the previous sections, but they find a proper place in a book of this nature, since they are produced on the fibre by oxidation of coal tar products. Some members are of the highest commercial importance and they are characterized by excellent fastness to light and washing. They find their chief application on vegetable fibres and are rarely applied to wool and silk.

The predominant member of this group of colours is aniline black, which is produced on the fibre by the oxidation of aniline oil or salts by methods described hereafter.

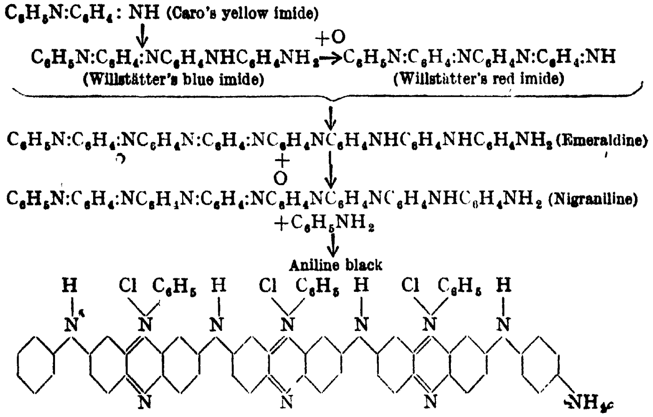
ANILINE BLACK

is one of the fastest blacks to light, washing and bleaching (single-bath aniline black is not fast to bleaching) known to the dyer. Its only rival in fastness is sulphur black, which will not stand bleaching. Both sulphur black and aniline black are extremely fast to light: the author has made prolonged comparative exposures of a prussiate aniline black and a sulphur black, but there was practically nothing to choose between the two after six months. Sulphur black is, however, much more quickly dyed than aniline black. The possible tendering of sulphur black is a disadvantage as compared with aniline black. The fibre is usually tendered to a certain extent when dyed with aniline black, but the tendering is definite and not progressive, whereas the tendering of sulphur black once it starts is progressive.

Aniline black is dyed in enormous quantities on cotton yarn, hosiery and cotton pieces: it is practically never dyed on loose cotton except on a sulphur black bottom, as detailed in Section VIII. Aniline black is not a commercial article, but is produced, as already mentioned, on the fibre by several different processes. The basis is aniline oil or aniline salts (aniline hydrochloride), which are supplied by the coal tar colour manufacturer in a state of high purity. The manufacture of both the oil and hydrochloride have been firmly established in Great Britain for many years, and in this branch of chemical manufacture the British product has always held its own against that of Germany.

The industrial application of aniline black was discovered and developed by John Lightfoot of Accrington, and it was at the Broad Oak Print Works of that town in which the first pieces were printed with aniline black. The methods employed by Lightfoot form the basis of modern practice. In his book entitled "Chemical History and Progress of Aniline Black" a full account of his work on this subject is given, to which the reader is referred for further details. Lightfoot's first patent on the subject was E.P. 151, 1863. It is interesting to note that aniline oil was a chemical curiosity at that time, and cost 15–20*s*. a pound against a pre-war price of 4½*d*.

Aniline black has always held a strong fascination for the chemist, both from a commercial and scientific point of view, so that the literature on the subject is sufficient to fill volumes. The classical work of E. Noelting and A. Lehne has been published in English, and their book on "Anilin Schwarz" gives a detailed study, to which the reader may refer. The constitution of aniline black was established by A. G. Green and his collaborators in 1913, when it was shown that the oxidation of aniline to aniline black may be assumed to proceed by a series of "quinonoid" additions, according to the following scheme :—



$C_6H_5N{:}C_6H_4{:}NH$ (Caro's yellow imide)

$$\downarrow \quad +O$$

$C_6H_5N{:}C_6H_4{:}NC_6H_4NHC_6H_4NH_2 \rightarrow C_6H_5N{:}C_6H_4{:}NC_6H_4N{:}C_6H_4{:}NH$

(Willstätter's blue imide) (Willstätter's red imide)

$$\downarrow$$

$C_6H_5N{:}C_6H_4{:}NC_6H_4N{:}C_6H_4{:}NC_6H_4NC_6H_4NHC_6H_4NHC_6H_4NH_2$ (Emeraldine)

$$+O \quad \downarrow$$

$C_6H_5N{:}C_6H_4{:}NC_6H_4N{:}C_6H_4{:}NC_6H_4NC_6H_4NC_6H_4NHC_6H_4NH_2$ (Nigraniline)

$$+C_6H_5NH_2 \quad \downarrow$$

Aniline black

For the arguments and experimental data for the above formulae the original paper must be consulted (*J.S.D.C.*, 1913, pp. 105 and 338).

The formation of aniline black by the acid oxidation of aniline oil proceeds in three well-recognized stages in practice. The first stage results in the formation of emeraldine, of which the free base is blue but its acid salts are bottle green, which is the colour of the cotton as it comes out of the "ager" when being dyed aniline black by the ageing process. The second stage of the oxidation converts the emeraldine into nigraniline, of which the free base is dark blue and the salts blue. Nigraniline is immediately reduced by sulphurous acid to emeraldine, which results in the black being turned green. The final stage of the oxidation converts the nigraniline into the so-called ungreenable aniline black because it is not reduced by sulphurous acid to emeraldine: when reduced by hydrosulphite ungreenable aniline black changes to brown, which on exposure to the atmosphere is reconverted into black.

The above reaction of nigraniline and ungreenable aniline black has given rise to the terms greenable and ungreenable black. The way in which an aniline black behaves to sulphurous acid is a test as to whether the aniline black has been fully developed: if it turns green the black still contains nigraniline, and has not been fully converted. One bath aniline blacks are turned green, but properly dyed aged and steam aniline blacks are ungreenable. It is, therefore, a common trade test to submit aniline blacks to a sulphurous acid treatment in order to determine whether it will turn green or not. An aniline black dyer is judged successful or otherwise according to whether his results turn green or not.

Aniline black is dyed on the commercial scale by three distinct processes, viz.:—

1. Single bath aniline black.
2. Aged aniline black.
3. Steam aniline black.

Before giving recipes for the above three processes it is necessary to explain that the recipes for aniline black are legion, therefore the recipes given hereafter are capable of being varied within wide limits.

The successful dyeing of aniline black on the big scale calls for great skill and constant attention on the part of the dyer to obtain satisfactory results without tendering the cloth. Aniline black demands the presence of mineral acid for its production, so that it will readily be seen that there is always a danger of tendering the material. Local conditions in processes 2 and 3 play a very important part, so that a recipe which is satisfactory in one dyehouse often turns out unsatisfactory in another dyehouse. Recipes have to be altered to meet these conditions, which explains the variation to be found.

SINGLE BATH ANILINE BLACK.

This process is the easiest to carry out, but the least satisfactory in its results. The black is fast to light and milling, but is turned green by sulphurous acid, always rubs, and is not fast to bleaching. Despite these drawbacks large quantities are dyed on yarn—particularly for the Eastern export trade: it is but rarely dyed on loose cotton or piece goods.

The shade produced is controlled by three factors—

1. Proportion of liquor to material.
2. The temperature to which the dyebath is raised.
3. The aftertreatment to which it is submitted.

The higher the proportion of liquor to material, the more aniline oil is required for the same depth of shade. The following recipe is a typical one for a single bath aniline black:—

For 100 lbs. cotton yarn—

10 lbs. aniline oil.
10 lbs. spirits of salts.
10 lbs. iron liquor.
10 lbs. D.O.V.
20 lbs. sodium bichromate.

The bath is made up as follows: the bichrome is dissolved in hot water and added to the cold dyebath, next the iron liquor, then the D.O.V., and stir the bath well. The aniline oil and spirits of salts are mixed together in a bucket along with a little water to keep the fumes down. The mixture is stirred until the aniline is completely dissolved. This operation is best carried out in the open air because the fumes are poisonous, and inhalation of the same should be avoided. This solution of aniline hydrochloride is added to the dyebath immediately before the yarn is entered into the bath. It must not be added to the bath and then time allowed to elapse before the yarn is entered, because immediately the aniline is added, the formation of aniline black commences, which would simply be precipitated in the dyebath and be wasted. After the yarn is entered work for one hour cold, and then raise slowly up to the boil, lift out and wash off thoroughly to remove all acid. The temperature to which the bath is raised plays an important part in the ultimate shade of black obtained.

If the temperature is only raised to 140° F. (60° C.), the shade is much redder than if it is raised to the boil, but the latter will be dustier. After washing off the yarn is either soaped or treated with an emulsion of oil, which improves the shade considerably. Alkali reddens the shade, so that, unless a bronzy shade is required, it should not be used in after-treating aniline black.

A large quantity of aniline black yarn is exported from Great Britain to the East: the author has dyed large quantities for this purpose to the following two recipes:—

Aniline Black Bronze Shade.—For 100 lbs. cotton yarn—

4½ lbs. aniline oil.
4½ lbs. spirits of salts.
4½ lbs. D.O.V.
4½ lbs. iron liquor.
9 lbs. bichrome.
120 gallons water.

Enter the yarn cold, work one hour cold, raise up to 140° F. (60° C.) in half an hour, wash off, then soap for half-hour at 140° F. (60° C.) with 10 per cent. soap, ½ per cent. soda ash.

Aniline Black Dead Shade.—For 100 lbs. cotton yarn—

5 lbs. aniline oil.
5 lbs. spirits of salts.
5 lbs. D.O.V.
5 lbs. iron liquor.
10 lbs. bichrome.
120 gallons water.

Enter the yarn cold, work one hour cold, raise up to boil in half an hour, wash off, then soap for half-hour at 140° F. (60° C.) with 10 per cent. soap.

The dead shade was always much dustier and dirtier than the bronze shade.

On first entering the yarn into the bath it is yellow—

the colour of the bichrome solution—which colour gradually turns green and finally black. Blacks dyed this way are turned green by sulphurous acid: they are not fast to chlorine and rub badly. They are fast to light and milling.

AGED ANILINE BLACK.

This process is applied the most largely of the three processes for dyeing as distinct from printing. It is used for pieces, hosiery and yarn, and yields an excellent shade of black which is fast to light, washing and bleaching, whilst it is not turned green by sulphurous acid.

The principle of this process consists in impregnating the cotton with aniline salts, an oxidizing agent, an oxygen carrier, and a hygroscopic substance. The oxidizing agent which is almost universally used is sodium chlorate, which is to be preferred to the potassium salt owing to its greater solubility. The oxygen carriers employed are copper sulphide, copper sulphate and vanadium chloride. The hygroscopic substance used is ammonium chloride, and its function is, by its hygroscopicity and dissociation at the temperature of the ager to start the reaction.

The following recipes are only given as typical recipes, which may be varied to suit local conditions obtaining—

Aniline Black with Copper Sulphate.—This recipe gives a fast to bleaching aniline black on yarn.

Use wooden or stone vessels throughout; no metal must be present.

Dissolve—

60 parts aniline salt in 320 parts water, and make perfectly neutral, if necessary, by addition of aniline oil.
2¾ parts copper sulphate in 50 parts water.
19 parts sodium chlorate in 37 parts water.
2 parts ammonium chloride in 12 parts water.
24 parts aluminium acetate 15° Tw.

Mix together and the resulting liquor will stand about 12° Tw. Pad the yarn in this liquor 2 lbs. at a time, and wring out so that it holds its own weight of liquor. Dry in a stove at 95° F. (35° C.) on sticks which have been saturated with the above liquor in order to avoid stick marks: turn the yarn every two hours (the workman must have dry hands, wet hands will make finger marks): when dry, let steam into the stove till the dry bulb shows 95° F. (35° C.), and the wet bulb shows 86° F. (30° C.). Keep at this temperature for six hours, by which time the yarn should have turned to a dark bottle green: chrome quarter-hour at 180° F. (80° C.) with 4 per cent. bichrome and 1 per cent. sulphuric acid, which treatment turns the yarn to a jet black, wash off and finally soap quarter-hour at 180° F. (80° C.).

Aniline Black with Copper Sulphide.—Copper sulphide in the form of a paste is used as the oxygen carrier, and is made by the double decomposition of copper sulphate and sodium sulphide as follows: 37½ parts copper sulphate are dissolved in 150 parts water, to which is added 39 parts sodium sulphide crystals in 100 parts water; filter and press the paste till it yields 54 parts, in which concentration it is used.

15 parts aniline salts made neutral with aniline oil.
5 parts copper sulphide paste.
5 parts sodium chlorate.
75 parts water.

100

The strength of the padding liquor is determined by the quality of the cloth. The cloth should be so squeezed that it retains its own weight of padding liquor. The cloth is dried, given a three-minutes' passage through the ager at 140° F. (60° C.), then chromed and soaped. The black may also be developed by hanging, when it naturally takes much longer, but the danger of tendering is greatly minimized.

Aniline Black with Vanadium Chloride.

8	parts aniline salts.
1½	parts aniline oil.
4	parts sodium chlorate.
5	c.c. vanadium chloride solution,
81½	parts water.
100	

The cloth is padded with the above, dried and developed by a two-minutes' passage through the ager at 200° F. (95° C.), or by hanging. A subsequent treatment with bichrome is not necessary.

Vanadium chloride solution is made as follows :—

8 grs. vanadate of ammonia are dissolved in 40 grs. spirits of salts and 80 c.c. water, then reduced by warming with 10 grs. glycerine till the solution turns blue, then dilute with water to 2 liters.

The amount of vanadium required is extraordinarily small: it has the drawback, however, compared with copper sulphide, that being soluble the padding liquor commences to oxidize much more quickly and therefore it is not so stable. Copper is therefore much more largely used than vanadium.

Green's Aniline Black Process.—In 1907 Green took out a process by which it was claimed to be possible to avoid tendering of the fibre. As far as the author's knowledge goes, it has not been adopted commercially in Great Britain. The patent is, however, given *in extenso*, since the process is interesting.

The invention relates to the production of an aged aniline black in dyeing or printing, the new process differing from all other known processes by the fact that the oxidation of the aniline is effected solely or mainly by the oxygen of the air. The possibility of dispensing with an oxidizing agent and thus of avoiding the tendering or weakening of the fibre due to oxycellulose formation, depends on the discovery that the addition of a small quantity of a paradiamine or of a para-amidophenol to a mixture containing aniline and a suitable oxygen carrier, such as a salt of copper, greatly accelerates the oxidation of the aniline by atmospheric oxygen.

Further, whereas in the ordinary processes of producing an "aged" black the quantity of mineral acid employed cannot be materially reduced below the proportion of one equivalent to one equivalent of base, under the new conditions here set forth a mixture which is strongly basic, containing, for instance, as little as half an equivalent or less of hydrochloric acid, may be used with satisfactory results. Still further, the hydrochloric acid or other mineral acid may be wholly or in part replaced by an organic acid, such, for instance, as formic acid, without materially affecting the quality of the black obtained. In either case, whether a basic mixture is employed or a mixture containing an organic acid, the tendering of the fibre by free mineral acid liberated during ageing or steaming is avoided, even when these operations are unusually prolonged. As suitable oxygen carriers, the chlorides of copper have been found to give the best results, and in order to prevent the premature formation of oxidation products in the padding or printing mixture, it has been found preferable to employ the copper in the form of a cuprous salt. A convenient method of effecting this is to add to the mixture cupric chloride or other cupric salt, together with a sulphite or bisulphite in quantity sufficient to reduce the cupric salt to the cuprous state, and a sufficient amount of a soluble chloride such as sodium, potassium, or ammonium chloride, to keep the cuprous chloride in solution. Mixtures thus prepared are quite stable and remain clear and colourless on exposure to air for a considerable period. Just as in the ordinary method of producing aniline black, so here also the aniline may be replaced wholly or in part by toluidine or meta-xylidine.

The mixtures composed as above are applied to textile fibres and fabrics in the usual manner, namely, by padding or printing. In the latter case the mixture is suitably thickened. The black is then developed by exposure of the material to air, which may be effected either by passage through the ordinary rapid ager, by hanging in a moist atmosphere, by steaming, or by any other convenient means. Finally, the material is washed and dried; or it may be subjected to a final oxidation by means of bichromate or to any other aftertreatment which is deemed desirable either to modify the shade or to render the black less liable to "green."

Amongst the paradiamines and the para-amidophenols suitable for this purpose the following are mentioned:—Paraphenylenediamine and its sulphonic and carboxylic acids, para-amidophenol, dimethylparaphenylenediamine, para-amidodiphenylamine, benzidine, diamido-diphenylmethane, quinone monoimide, quinone di-imide and their chlorides, paranitrosophenol, nitrosodimethylaniline, para-amidophenyl-quinonimide, and their analogues, homologues, or derivatives.

The following examples are given:—

(1) The padding mixture is prepared by adding a solution composed of 48 parts cupric chloride, 140 parts ammonium chloride, and 14 parts sodium meta-bisulphite in 500 parts cold water, to a solution composed of 50 parts aniline, 2 parts paraphenylene-diamine, 15 parts hydrochloric acid (30 per cent.), and 15 parts formic acid (90 per cent.) in 1,500 parts cold water.

(2) The padding mixture is prepared by adding a solution prepared as in example (1) to a solution composed of 50 parts aniline, 4 parts paraphenylenediamine, 30 parts formic acid (90 per cent.), in 1,500 parts cold water.

(3) The padding mixture is prepared by adding a solution prepared as described in the first part of example (1) to a solution composed of 50 parts aniline, 4 parts paraphenylenediamine, and 50 parts hydrochloric acid (30 per cent.) in 1,500 parts cold water.

It is claimed that by the new process a fuller utilization of the aniline is rendered possible, the danger from spontaneous inflammation is removed, the risk of injury to the workpeople is greatly diminished, the manufacture is simplified, and greater speed of production is attainable. The action of the paradiamine or para-amidophenol is believed to be a catalytic one, since the quantity employed need only be small in proportion to the aniline, and may be varied within wide limits. It is thought that these substances bring about the oxidation of the aniline by intermediate formation of complex indamines, from which they are constantly regenerated.—Engl. Pat. No. 16189, 1907.

STEAM ANILINE BLACK.

This third process for the production of aniline black is more largely used in calico printing than in dyeing, though this process is used for dyeing pieces. The black produced by this method is reputed to be less greenable than the "aged" black, whilst the danger of tendering the fabric is also less. The padding liquor may also be kept longer without formation of aniline black. It does not develop so far in the steaming as an aged black and therefore requires to be well after-chromed. The following is a typical recipe:—

I. { 84 parts aniline salt neutralized, if necessary, with aniline oil.
300 parts water.

II. { 49 parts yellow prussiate of potash dissolved in
300 parts water.

III. { 27 parts sodium chlorate dissolved in
300 parts water.

Dissolve each ingredient separately and when required mix together in equal portions. Pad, dry, steam 2-3 minutes, then chrome at 120° F. (50° C.) with ½ lb. bichrome per 10 gallons.

DIPHENYL BLACK.

This product was introduced by Meister, Lucius and Brüning in 1892 (*D.R.P.* 134559), and consisted of amido-diphenylamine, which was marketed as diphenyl black base and also diphenyl black oil DO, which consisted of one part amido-diphenylamine dissolved in 3 parts aniline oil. The advantages claimed for this black over aniline black were—

1. The black was absolutely ungreenable.
2. The fibre was not tendered in the least degree owing to the absence of mineral acid, whereas aniline black requires mineral acid for its development.

Owing to the considerably higher price of the product as compared with aniline oil its introduction has not proved a serious rival to aniline black.

The following are the recipes for piece dyeing given by the makers :—

A Diphenyl Black Base.

Standard A
60 parts tragacanth water 1 : 10.
75 parts water.
40 parts diphenyl black base dissolved in
50 parts lactic acid 50 per cent., and
130 parts acetic acid, 40 per cent., are stirred into the tragacanth after cooling and made up to 500 parts with water.

Standard B
25 parts aluminium chloride 52° Tw.
25 parts chromium chloride 52° Tw.
4 parts copper chloride 76° Tw.
340 parts water are mixed with
30 parts sodium chlorate dissolved in
60 parts hot water and
10 parts turpentine.

Equal portions of A and B are mixed together. The standard solutions are stable, and no more should be mixed than can be used each day.

Pad the cloth to hold its own weight of liquor, dry, steam 2 minutes at 212° F. (100° C.), wash and soap at 140° F. (60° C.). Chroming is not necessary, in fact it is detrimental, as it depreciates the shade.

ANILINE BLACK ON WOOL AND SILK.

Aniline black does not develop on wool and silk like it does on vegetable fibres due to the reducing action of the fibre. The production of aniline black on wool has attracted many investigators—notably Kallab—but it has never been made a commercial success. Indeed the author can see no place for aniline black—as such—on wool, seeing the very satisfactory range of fast chrome blacks available, which practically meet all the requirements of the wool dyer.

There is, however, one special application to wool and silk which should be included here. It is confined to silk and mohair pile fabrics, and is used for producing chinchilla and black shades with white tips, and is carried out as follows :—

Black—

5 parts potassium permanganate.
7 parts zinc or magnesium sulphate.
100 parts water.

Work cold in this solution 15 minutes, then raise up to 120° F. (50° C.) in half-hour : wash off and dry. The object of the zinc or magnesium sulphate is to immediately neutralize the caustic soda which is liberated by the permanganate of potash and so prevent it acting on the wool or silk. This bath dyes the fibre a dark brown due to the precipitation of oxides of manganese on the fibre.

In order to produce white tips the oxides of manganese are discharged by what is termed a " cutting liquor " made up as follows :—

3 quarts hydrogen peroxide.
1 pint acetic acid.
1 oz. oxalic acid dissolved in 1 pint water.

This is suitably thickened to prevent it running on the fibre when brushed on. Girls specially trained to the work brush the cutting liquor on in any desired design. After the fabric has dried the black is developed by working for ten minutes cold in a bath containing—

$$\begin{array}{l} \text{1000 parts water.} \\ \left.\begin{array}{l}\text{5 parts aniline oil} \\ \text{5 parts D.O.V.}\end{array}\right\}\text{ mixed together.}\end{array}$$

The fabric is not black when it comes out of the bath, but the development of the black is completed by soaping with the addition of a little ammonia at 100° F. (40° C.). Wherever the cutting liquor has been brushed on the colour will not have developed, so that the fibre is white.

Chinchilla effects are produced on exactly the same lines by reducing the quantities of permanganate and aniline oil employed.

GENERAL NOTES.

The cotton must be thoroughly cleaned by a preliminary boiling out with alkali before being dyed aniline black. It must, however, be washed free from the alkali, because alkali prevents the formation of aniline black. Free mineral acid is necessary for the formation of aniline black.

A large amount of research has been done on amines other than aniline, but none have proved to give such good results. Amido-diphenylamine (diphenyl black base) may be mentioned as the best.

It has been shown that it is necessary to have free aniline present in the last stage of oxidation in order to produce ungreenable aniline black. This explains why aniline salts are sometimes added to the chrome bath.

Cotton dyed with aniline black usually gains in weight with a maximum gain of 10 per cent.

Aniline black is often dyed on top of sulphur blacks (see p. 112). It is less frequently dyed on top of direct cotton blacks.

106 parts aniline salts correspond to 76 parts of aniline oil.

Lehne recommends the following reagent for testing aniline black for liability to turn green: 20 c.c. sodium bisulphite 70° Tw., 20 c.c. hydrochloric acid 34° Tw., 500 c.c. water. Work 10 minutes cold in this, wash, dry and compare with untreated pattern.

Paramine Brown, Fuscamine Brown, Ortamine Brown.

The above browns are produced on the fibre in an analogous way to aniline black from—

Paramine (paraphenylene diamine), D.R.P. 176062, 1904.
Fuscamine G (meta-amido phenol), D.R.P. 210643, 1908.
Ortamine D (ortho-di-anisidine), D.R.P. 250466, 261871.

The above products were put upon the market through the work of Henri Schmid of Mulhouse, who developed the recipes given below. It will naturally be thought that this would have been carried out earlier, but all results obtained by using the hydrochlorides in similar manner to aniline salts were not practicable, due to the corrosion of the fibre, though the shades obtained were particularly fast.

The following processes yield shades fast to light and washing, whilst they have the additional advantage of being easily discharged which makes them of special advantage in calico printing. Paramine gives a red chocolate brown, whilst fuscamine and ortamine give yellow-brown and biscuit shades.

Padding liquors are made up according to the following recipes :—

Paramine Brown—

20 grs. paraphenylene diamine are dissolved in
250 c.c. hot water, then diluted with
450 c.c. cold water.
1½ grs. rongalite C are now added to prevent oxidation
of the paraphenylene diamine, then add
20 grs. sodium chlorate dissolved in 50 c.c. water,
20 grs. ammonium chloride dissolved in 50 c.c. water,
30 c.c. tartar emetic glycerine solution.

Make up to 1 liter with cold water. Filter, then add just before use, 0·015 gr. ammonium vanadate.

The tartar emetic glycerine solution increases the stability of the above padding liquor, and is made up as follows :—

40 grs. tartar emetic,
340 grs. glycerine,
620 c.c. hot water.

Fuscamine Brown—

20 grs. meta amido phenol,
20 grs. hydrochloric acid 30° Tw.,
400 c.c. water.

25 grs. sodium chlorate,
100 c.c. water.

5 grs. potassium ferrocyanide,
100 c.c. water.

Mix together and make up to 1 liter.

Ortamine Brown—

28 grs. ortho-di-anisidine,
7 grs. hydrochloric acid 30° Tw.,
20 grs. formic acid 90 per cent.

Reduce the ortho-di-anisidine to a paste with water, add the acids and warm till dissolved, allow to cool, add 20–25 grs. sodium chlorate, make up to a liter, filter, add as a catalyst—

0·4–0·6 per cent. potassium ferrocyanide or ferrous sulphate.

Pad with any of the above solutions, dry at 100–120° F., steam 3–5 minutes, soap, wash and dry.

Paramine brown is a red chocolate brown which is not so popular as a yellower shade; fuscamine and ortamine brown are yellower shades. The three products are miscible one with another, which enables a large range of brown and biscuit shades to be obtained.

FUR DYEING.

This is a special branch of dyeing which falls in this section, since furs are largely dyed by the oxidation of coal tar products on the fibre. The three bases which are most commonly used for fur dyeing are paraphenylene diamine, para amido phenol, and ortho amido phenol: pyrogallic acid is used to a lesser extent.

Owing to pelts being so sensitive to heat the ordinary processes of dyeing are inapplicable, therefore fur dyeing is carried out cold in order to preserve the pelts. The products enumerated above are put on the market under several fancy names, such as Ursol, Nako, Furrol, &c. Paraphenylene diamine is the most important product for black dyeing.

The dyeing of furs is a difficult branch of dyeing which requires great skill, coupled with experience and knowledge of the furs. The preliminary process in fur dyeing is technically called "killing," which is in reality a degreasing operation, so that the individual fibres will be in a fit condition to absorb the mordant and dye liquors. The chemicals used for this purpose are lime and soda, the former giving the better result. The skins are soaked for 2 hours in a cold bath containing 1 lb. lime to 10 gallons water. They are then thoroughly washed to remove all lime previous to mordanting.

From the dyeing point of view furs may be roughly divided into two classes, viz.: —

1. Sheepskin, Persian goat, kid, kid-cross, schmasche, lamb, and allied skins.

2. Rabbit, hare, fox, opossum, musk, goat (long-haired as distinct from the Persian goat), and allied skins.

The distinction between these two classes is that the individual fibres of the former have a much greater absorbing capacity or penetrability than the latter.

The principle of this method of fur dyeing is the oxidation on the fibre of the bases enumerated above. This is carried out by first mordanting the skins with an oxidizing agent. Bichrome, copper sulphate and iron salts are the three chief mordants used. Light shades are dyed without previous mordanting, but dark shades are usually first mordanted. Hydrogen peroxide is the oxidizing agent used in the dyebath itself and is added to the dyebath after the fibre has become thoroughly saturated with the base.

Paraphenylene diamine is the base most commonly used in fur dyeing, but the workpeople must be well protected from it or they are liable to contract skin diseases and poisoning.

Black with Paraphenylene Diamine.—Make up a 1 per cent. solution of paraphenylene diamine and make it acid with acetic acid. Work the furs in this at 100° F. (40° C.) until they are thoroughly saturated, then add 5 c.c. hydrogen peroxide (10 vol.) for every gram of paraphenylene diamine, allowing the bath to gradually fall to normal temperature. The furs will gradually develop to a full black, provided the bath is kept on the acid side with acetic acid throughout. A full black will be developed in 8–10 hours.

A modified recipe is as follows :—

5 lbs. paraphenylene diamine are dissolved in boiling water, then made up to 7½ gallons with cold water : make slightly acid with acetic acid, cool and add 2½ gallons hydrogen peroxide (10 vol.). If this is brushed on and allowed to stand, it will produce a black.

Brown with Paraphenylene Diamine.—Proceed as above, except that the bath is made alkaline with soda ash, when a brown instead of a black is obtained.

Fur dyeing has for its chief object the colouring of inferior skins to look like the more expensive and rare skins, such as sable, etc. In order to produce the markings on the natural furs the solutions of the various bases mixed with hydrogen peroxide, already described, are brushed on in as close an imitation as possible of the genuine article.

SECTION XII.—OTHER USES OF COAL TAR DYESTUFFS

IT is only to be expected that coal tar dyestuffs find employment in many other industries in addition to that concerned with the dyeing of textile fibres. It has been thought advisable to include in this volume a short *résumé* of these other uses. The consumption of coal tar dyestuffs is very large in some of these industries, *e.g.* lake and paint manufacture, whilst it is just as small in other industries, *e.g.* medicinal uses.

The following summary will enable the reader to gather how widespread is the use of coal tar dyestuffs :—

Calico Printing.—All classes of colours are used for the many and varied styles which are employed in this industry. Those mordant dyestuffs which may be printed with acetate of chrome meet with a very large consumption, whilst para red styles are an important branch of this industry. It would require a volume as large—if not larger—than the present one to deal adequately with this subject. Those who are desirous of studying the methods used in this industry are recommended the following volumes :—

"The Principles and Practice of Calico Printing." Knecht and Fothergill.

"The Colour Printing of Carpet Yarns." Paterson.

"Bleaching and Calico Printing." Duerr.

"Aniline Black and its Application in Dyeing and Printing." Noelting and Lehne.

Lake and Paint Manufacture.—The consumption of dyestuffs in these two industries is extremely large for the following purposes :—

1. Oil paints.
2. Lime colours for distempers.
3. Lakes for wallpapers and coated papers.
4. Printing and lithographic inks.

These industries use selected dyestuffs from the basic, acid, mordant, resorcine and insoluble azo classes of dyestuffs. This industry, like calico printing, would require a volume to deal adequately with the methods employed. Those who are desirous of studying these methods are recommended the following books :—

" The Chemistry of Pigments." E. J. Parry and J. H. Coste.

" Oil Colours and Printers' Inks." L. E. Andé.

"The Manufacture of Mineral and Lake Pigments." J. Bersch.

" Modern Printing Inks." A. Seymour.

" The Manufacture of Lake Pigments from Artificial Colouring Matters." F. H. Jennison.

Soap Colouring.—Selected dyestuffs are largely used for the colouring of toilet soaps. The dyestuffs employed are those which will withstand weak alkali. Amongst the dyestuffs employed may be enumerated : quinoline yellow, tartrazine, citronine, acid oranges, rhodamines, acid scarlets, direct cotton browns, violets, greens, etc.

Typewriter Ribbons, Carbon Papers.—Methyl violet, malachite green, victoria blue, eosine, nigrosine are the chief dyestuffs used for this purpose. The colours are used both in their oil soluble and water soluble forms, according to whether they are to be mixed with oil or glycerine, etc. The colours used are required to be as soluble as possible, so that they will give the maximum number of copies.

The colours are ground with the oil, spirit or glycerine in special machines fitted with granite rollers till the mass is homogeneous. It is then applied to the tapes or papers.

Copying Ink Pencils.—The chief dyestuff used for this purpose is methyl violet, which is ground up with graphite to make the lead. Other dyestuffs used are victoria blue and malachite green.

Spirit Varnishes and Lacquers.—The dyestuffs which are used for these purposes have to be soluble in methylated spirits. The basic dyestuffs, which are all soluble in methylated spirits, find employment together with the Sudan colours, *i.e.* monoazo dyestuffs, which do not contain sulphonic acid groups, such as aniline coupled with β naphthol: spirit blue, induline and nigrosine are also largely used, *i.e.* rosaniline blue, induline and nigrosine before they are sulphonated. The introduction of sulphonic acid groups into the colour molecule usually makes the molecule insoluble in methylated spirits, though there are exceptions to this, *e.g.* sulphonated rosaniline blues (commercially known as soluble or water blues) are soluble in methylated spirits, though not as freely as the unsulphonated base. Details of varnish and lacquer manufacture will be found in—

"The Manufacture of Varnishes and Kindred Industries." Livache and McIntosh.

"Recipes for the Colour, Paint, Varnish, Oil, Soap and Drysaltery Trades." Scott, Greenwood, & Co.

Writing Inks.—The use of coal tar dyestuffs in the manufacture of writing inks fulfils two definite and distinct purposes. Some are used for making coloured inks, whilst others are used for "sighting" iron-gall inks pending the full development of the iron tannate by oxidation by the atmosphere. Of the colours used for making coloured inks the following may be mentioned: eosine for red ink, malachite and brilliant green for green ink, nigrosine and acid black for cheap black inks.

Better quality inks depend upon the development of iron tannate for their final colour. They are made from decoctions of gall nuts and copperas (ferrous sulphate): in order to make the writing visible a little pure blue or soluble blue is added. This colour is chosen because it is not precipitated on long standing with tannin, whereas many dyestuffs are.

The modern development of ink manufacture is to supply the ink in powder form. These powders have many advantages. They reduce transport, avoid breakages, also reduce loss through evaporation in hot countries. They are supplied in small canisters in quantities sufficient to make definite quantities by addition of cold water. These powders consist of carefully calculated mixtures of tannin, copperas and dyestuff, with minute quantities of salicylic acid as a preservative. Carbolic acid is used as a preservative in fluid inks.

The following is a recipe for a tannin-iron ink :—

Dry pure tannic acid	23·4
Crystallized gallic acid	7·7
Ferrous sulphate	30·0
Gum arabic	10·0
Hydrochloric acid	2·5
Carbolic acid	1·0

Make up to 1000 with water and add sufficient pure or soluble blue to make it visible on first writing.

Marking Inks.—Many of the modern marking inks are made upon a basis of aniline black (see Section XI.). These inks are of two classes, viz. inks which develop rapidly and inks which develop in the course of 24 hours. The following recipe belongs to the latter class, and the author can vouch for its excellence from many years' experience of it, nor does it rot the fabric :—

Solution A—

Copper chloride	85
Sodium chlorate	106
Ammonium chloride	53
Water	600

Solution B—

Glycerine	30
Gum	20
Water	40
Aniline salts	60
Water	90

Mix together 1 part A with 4 parts B just before use : the ink takes 12–24 hours to develop, after which it will resist modern laundry treatment.

The following book on writing inks may be recommended :—

"Ink Manufacture," by S. Lehner.

Coloured Waxes.—This class includes boot polishes and allied preparations, such as leather dressings, quick stains for leather soles, etc.

A limited number of coal tar dyestuffs are soluble in oils, waxes, turpentine, etc., and they are specially prepared for this purpose. The basic dyestuffs in their commercial form are not soluble in oil, but if they are first treated with caustic soda to liberate the free colour base, the colour base will dissolve in oil. They are put on the market by the colour manufacturers in the form of the free colour base, under the names of oil red, etc., or violet base, etc. Nigrosine and induline in the base form are oil soluble, whilst the Sudan dyestuffs are also soluble in oil.

These same colour bases are freely soluble in petrol, benzol, toluol, etc., and are sometimes used for colouring these spirits for detection purposes. A recent development in the use of these spirit soluble colours which is due to the war is their employment in the colouring of aeroplane dopes.

There is a large consumption of coal tar dyestuffs in shoe polishes, leather dressings, etc. The above class of oil soluble dyestuffs are used if it is a turpentine cream, whilst water soluble dyestuffs are used for saponified creams. For blacks nigrosines oil and water soluble are used: for tans Bismarck brown and phosphine oil and water soluble are used. The following are typical recipes of the two classes of boot creams :—

Turpentine cream—

Grey carnauba wax ..	10 parts
Paraffin scale	23 parts
Turpentine	70 parts

Colour with oil soluble black or brown as desired.

Saponified cream—

Grey carnauba wax ..	5 parts
Beeswax	5 parts
Japan wax	8 parts
Potassium carbonate ..	5 parts
Water	80 parts

Melt the wax in an open pan, add the alkali dissolved in half the water and the warm solution is stirred into the melted wax, taking care not to add too much at a time, or the mixture will froth up unduly. Heating must be continued until the wax is emulsified, the rest of the water added, and the mixture stirred till uniform. Colour with water soluble nigrosine, Bismarck brown, or phosphine, according to shade desired.

Food Colouring.—Coal tar dyestuffs are largely used in the colouring of many food preparations and liquors, amongst which may be enumerated egg powder, custard powder, blancmanges, jellies, chocolates, wines, lemonade, mustard, fried fish batter, ices, butter, etc.

Dyestuffs which are used in Great Britain must conform to the Foods and Drugs Act as regards contents of arsenic, etc.; provided, however, that they do not contravene the above Act there are no restrictions on which dyestuffs may be used.

The United States Department of Agriculture have, on the contrary, investigated the effects of coal tar dyestuffs in food preparations very thoroughly. As the result of investigations carried out by Dr. Bernard C. Hesse the use of the following dyestuffs was legalized, coupled with the exclusion of all others: amaranth, scarlet 3R, erythrosin, orange I, naphthol yellow S, tartrazine, light green SF, yellowish and indigo di-sulphonic acid. The same department has just issued Bulletin No. 448, entitled "Separation and Identification of Food-colouring Substances," by W. E. Mathewson. In this bulletin methods are detailed for the detection and identification of dyestuffs in food preparations.

All dyestuffs used for food colouring are required to possess great solubility, so that solutions made therefrom will not become turbid on standing. Many colourings are supplied to confectioners dissolved ready for use, which makes good solubility essential.

Indicators.—A few coal tar dyestuffs are used as indicators owing to their sensitiveness to acids or alkalies. Amongst those used may be mentioned: acid magenta;

alizarine, alizarine blue S, alizarine green B, alkali green, benzopurpurine B, congo red, croceine, dimethylaminoazobenzene, erythrosine, fast red, fluoresceine, magdala red, malachite green, methyl green, methyl orange, methyl violet, phenolphthalein, tropaeoline O, 2O, 3O. The behaviour and sensitiveness of the above dyestuffs as indicators have been tabulated by Salm and have been incorporated in " The Chemists Year Book." Atack.

Medicinal Uses.—Coal tar dyestuffs have long been used in the medical profession for microscopic stains, for which purposes specially purified dyestuffs have been marketed, notably by Grübler.

A recent development of the use of coal tar dyestuffs by the medical profession is for antiseptic purposes. Sensational announcements were made in the press of the recent discovery of the acridine dyestuff flavine by Dr. Browning as an antiseptic. The following statement was made by the Medical Research Committee in order to reduce the matter to its proper proportions :—

" The incomplete statements which have appeared from time to time in the Press with regard to the antiseptic 'flavine' have necessarily led to some misapprehension of the situation by the public. The impression has been created that flavine is a substance of magical potency, which can cure infected wounds. . . . It should be realized that no antiseptic, even a theoretically ideal antiseptic when that is obtained, can ever be more than an adjunct to skilled and thorough surgery. Flavine must be thought of accordingly in relation to other new antiseptics which have been brought into successful use during the war. These fall into two main classes : one depends upon the use of chlorine compounds . . . The second class to which flavine belongs include the elaborate compounds of which most are brilliantly coloured and are used as dyes."

Flavine, malachite green, brilliant green and acid scarlet R are all being used in the above connection at the present time.

SECTION XIII.—DYESTUFFS OTHER THAN COAL TAR DYESTUFFS STILL IN USE

THE dyestuffs still used in the dyeing industry which are not derived from coal tar belong to two classes, viz.:—

1. Vegetable dyestuffs.
2. Mineral dyestuffs.

To the first class belong logwood, fustic, cutch, Persian berries and cochineal: to the second class belong Prussian blue, iron buff, metallic oxide khaki, chrome yellow, chrome orange and manganese bronze. Of the above list of dyestuffs the use of Prussian blue, chrome yellow and chrome orange has declined considerably. Prussian blue possesses the drawback of being sensitive to alkalies, which turn the shade brown due to the formation of basic ferric hydrate. Chrome yellow and chrome orange are lead compounds, which are poisonous, so that their use is to be deprecated. Cochineal has also lost its importance since khaki has so largely supplanted the former red in military uniforms: its use is largely confined to the dyeing of scarlet for hunting coats. The other dyestuffs survive for sound economic reasons which will be indicated in discussing the individual dyestuffs.

VEGETABLE DYESTUFFS.

The war has had a most beneficial effect on the employment of vegetable dyestuffs due to the shortage of coal tar dyestuffs. Natural indigo, which was moribund on the outbreak of war, should strictly be included in this section, but since the methods of application are identical to those of synthetic indigo (Section IX.), there is no need to repeat them.

Logwood

is the wood of the tree known botanically as *Haematoxylin campechianum.* The colouring principle contained by it is haematoxylin, which yields on oxidation haematein, which is the colour which is fixed on the fibre. Logwood is put on the market in the form of chips, logwood extract, haematine paste and haematine crystals. They contain both haematoxylin and haematein. The mordant used is varied according to whether haematoxylin or haematein predominates.

Logwood is a dyestuff of many advantageous properties, and possesses a surprising universal utility. Its advantages are, it is very cheap: its shade possesses a beautiful bloom which has not yet been equalled by any synthetic dyestuff: it feeds the cloth: it covers the burls, whereas many coal tar blacks accentuate their prominence. It is very level dyeing and penetrates well.

Its disadvantages are its weakness to light as compared with afterchrome blacks; its sensitiveness to acids: it requires a mordant and does not adapt itself to use in modern dyeing processes, such as the metachrome and top-chroming processes (see pp. 54–62). Prior to its post-war revival there is no doubt that logwood was slowly but continually losing ground, the afterchrome blacks which are fast to potting being largely responsible for this state of affairs.

Its manifold uses will now be briefly indicated.

Silk.—Logwood has always maintained its position in black silk dyeing, since it not only gives a beautiful shade on silk, but it may be applied so that the silk is weighted to the extent of 200–300 per cent.

The following is a typical method of dyeing black on silk yarn which is abstracted from "Bleichen und Färben der Seide und Halbseide," by Carl H. Steinbeck. The recipes for logwood black on silk are very numerous, and are requisite for the different qualities of silk, shade of black, and amount of weighting required.

1. Bottom three times with basic ferrous sulphate 42° Tw., by working 1–2 hours in the cold bath.

2. Soap at the boil in an old soap bath.

3. Soap at the boil with 50 per cent. olive oil soap.

4. Treat with 25 per cent. potassium ferrocyanide and 32 per cent. hydrochloric acid, which gives the silk a bottom of Prussian blue to beautify the shade.

5. 90 per cent. cutch and 15 per cent. Glauber's salt. Enter at the boil, give three turns, allow the bath to cool to 120° F. (50° C.), add 15 per cent. stannous chloride, and work a further 1½ hours.

6. Wash off in three cold waters, and one at 120° F. (50° C.).

7. Dye in an old logwood bath, to which is added 25 per cent. logwood and 25 per cent. olive oil soap. Enter at 140° F. (60° C.), give five turns, raise to boil, and give seven turns.

8. Wash off in two cold waters.

9. Charge a cold bath with 10 per cent. hydrochloric acid, give seven turns, wash off, and wring out.

10. Prepare a bath of pyrolignite of iron at 4½° Tw. Enter cold, give seven turns, wring out, and allow to hang for 3 hours.

11. Prepare a bath with 25 per cent. cutch: work 1 hour at 95° F. (35° C.), wring out, and wash off with cold water.

12. Dye with logwood extract with addition of 7½ per cent. olive oil soap. Enter at 140° F. (60° C.), and work to shade at the boil.

13. Work ½ hour cold with 3 per cent. acetic acid.

14. Scroop with 5 per cent. acetic acid and 2 per cent. olive oil.

From the above recipe it will readily be seen what a lengthy process the dyeing of silk black with logwood is: some dyehouses therefore confine themselves to black dyeing only.

Wool.—Logwood used to be dyed on wool with the help of iron or chrome mordants: the former is but rarely used nowadays, though logwood on iron mordant is faster than on chrome mordant, since it is not so liable to turn green on exposure to the atmosphere. Copper sulphate improves the fastness to light, so that it is frequently combined with the above mordants or added direct to the dyebath towards the end of the dyeing operation.

Wool is mordanted with iron by boiling for 1½ hours with 4 per cent. ferrous sulphate, 2 per cent. copper sulphate, 8 per cent. argol, then allowed to lie overnight, which gives much better results than if dyed immediately. No doubt the ferrous oxide passes into a higher state of oxidation. Dyeing is carried out for 1–1½ hours at the boil.

An alternative process is to dye the wool first with the logwood, then to add the ferrous sulphate and copper sulphate to the dyebath after the logwood has gone on to the wool. The result is better if the ferrous and copper sulphates are applied in a fresh boiling bath.

An alternative method of applying logwood on iron mordant is a single bath process known as Bonsor's black, which is a popular way of dyeing logwood due to it being a single bath process. It depends on the principle that the logwood-copper-iron lake, which is insoluble in water, is brought into solution by means of oxalic acid. The bath is charged with the logwood, copperas and copper sulphate, then the precipitate is brought into an olive brown solution by the addition of oxalic acid. Dyeing is carried out for 1–1½ hours just below the boil. An excess of oxalic acid prevents the rapid development of the black, whilst too little oxalic acid may be detected by the colour of the bath not being olive brown, but of a green cast. The shade will also not be fast, but will rub, due to loose precipitate being fixed on the fibre owing to it not being in complete solution.

Logwood is most commonly dyed on a chrome mordant in modern dyeing practice. The choice of mordant depends on the degree of oxidation of the logwood being used. As previously stated, logwood as put on the market consists of haematoxylin and haematein. If the logwood contains a maximum of haematein then it is best dyed on a reduced mordant; if, on the other hand, it contains a maximum of haematoxylin it is best dyed on an oxidizing chrome mordant (*vide* p. 52). In testing logwood before buying it should be tested on the two following mordants :—

3 per cent. bichrome, 1 per cent. D.O.V.—oxidizing mordant.

3 per cent. bichrome, 2½ per cent. cream of tartar—reduced mordant.

If the better result is obtained on the oxidizing mordant it is evident that the logwood has not been fully "aged," and so should be dyed on an oxidizing mordant: the reverse result indicates the employment of a reduced mordant.

Logwood is very popular with the dyers because of its easy levelling and good penetrating powers. It may be applied on any of the chrome mordants detailed on pp. 52, 53, either as a self-colour or in conjunction with any other mordant dyestuff. When dyed alone 1 per cent. copper sulphate is frequently added after the dyebath is exhausted, to improve the fastness to light.

The one point to be observed in dyeing logwood is to avoid excess of bichrome in the mordant, because this deteriorates its fastness to light.

Logwood blues are obtained by dyeing on an aluminium or chromium mordant: they are fast to milling, but are not fast to light. They are, however, used as cheap indigo substitutes in the shirting trade, for which fastness to light is not of paramount importance. When dyeing blue with logwood the addition of calcium acetate to the dyebath is beneficial in enhancing the richness of the shade.

Logwood has another advantage from the dyer's point of view. If too much is got on the fibre the excess may be removed by a treatment with weak acid without damaging the wool.

Cotton.—Logwood has lost a great deal of its importance for cotton owing to the length of time required to dye it as compared with sulphur or direct cotton blacks, whilst sulphur blacks are immeasurably superior in fastness. The following recipe is one which has been used in practice :—

For 100 lbs. yarn—

3 gallons sumach extract,
250 gallons water.

Give 3 turns, steep overnight, wring up next morning. Sadden with

4½ gallons nitrate of iron,
250 gallons water.

Give 6 turns, wring up and pass through lime-water. Dye with—

10 lbs. solid haematine,
2 lbs. fustic extract.

Work 45 minutes at 185–212° F. (85–100° C.). Add 2 lbs. copperas, work ½ hour, wash off and soap with 10 per cent. soap at 140° F. (60° C.), hydroextract and dry.

Jute.—Logwood is still largely used in the jute trade for cheap blacks, which are blacks only in name compared with the popular conception of black, as they are really only greys. Since tannin is a natural constituent of the jute fibre a black is easily obtained by treatment with copperas, then logwood. Prior to the war logwood blacks were dyed on jute for ½*d*. and less per lb., so that it will be readily surmised that much money could not be spent on either material or labour.

Leather.—Logwood still finds extensive employment in leather dyeing both as a dyestuff and as a constituent of leather dressings. It is applied to leather in conjunction with ferrous sulphate, nitrate of iron or pyrolignite of iron. The logwood, usually deadened with addition of a little fustic, is brushed on the vegetable tanned leather, then the leather is subsequently brushed with ½ per cent. solution of ferrous sulphate. Chrome-tanned leather, since it contains no tannin, must be given a preliminary treatment with sumach extract before the logwood is applied.

The following is a typical recipe for a black seasoning for leather :—

2 oz. solid logwood extract,
¾ oz. copperas,

are dissolved separately, then mixed together to form a total volume of 3 quarts.

½ oz. glycerine } are mixed together, then added to the
1 pint milk } above.

Finally add
1 pint blood.

Logwood is also used for making stains for burls in woollen pieces. The following is a typical recipe :—

I. 2½ oz. solid logwood extract are dissolved in one gallon water.
II. ⅐ oz. soda ash } are dissolved in 1¾
⅛ oz. neutral potassium chromate } pints.

The boiling solution I. is slowly added to boiling solution II.: the mixture is boiled for 10–15 minutes, so that a clear blue-black solution is obtained. After cooling add 6½ pints methylated spirits.

FUSTIC

is the wood of a tree, the botanical name of which is *Morus tinctoria* or *Maclura tinctoria.* It is usually put on the market in the form of fustic extract. It is a yellow wood, which is employed for deadening the shade of logwood and as a mordant yellow which may be applied in conjunction with any other mordant dyestuff. It may be applied on any chrome mordant detailed on pp. 52, 53. Its great drawback is that it cannot be applied by the metachrome process (p. 59) or the topchroming process (p. 54). For this reason its use is declining. Despite the fact that it is not as fast to light as the best mordant yellows, it is a great favourite with dyers owing to its cheapness and its level dyeing properties on long locky wool.

CUTCH.

This product is also known as catechu and gambier. Gambier is a form of cutch in which the colouring principle is not in as high a state of oxidation. Gambier, therefore, shows a proportionately greater increase of colour on being treated with oxidizing agents such as bichrome and copper sulphate. It is extracted from acacia, areca and uncaria, which grow freely in India. It yields a brown shade which possesses very good fastness and has not yet been supplanted by coal tar dyestuffs owing to its fastness coupled with its cheapness. It imparts to cotton a distinctive hard handle, which is demanded in certain fabrics and which cannot be successfully imitated with coal tar dyestuffs. This same hard handle is the reason why cutch is practically never used for the dyeing of wool. It is freely used in conjunction with logwood for weighted blacks on silk (see p. 187). On cotton it is largely used for overall and sail cloth and on jute for ambulance stretcher cloth, whilst gambier is largely used for making brown papers.

Cutch is usually applied to cotton by the two-bath process, in which the cotton is first boiled with the requisite amount of cutch, to which is added 1–2 per cent. copper sulphate. The cotton is then squeezed off and developed in a fresh bath at 140° F. (60° C.), with 1–2 per cent. bichrome, which both fixes and developes the shade. The harsh handle given to cotton by cutch prevents its application to raw cotton owing to it breaking the teeth of the cards when being carded. It is usually, therefore, applied to cotton yarn or piece, not loose cotton.

Since cutch contains tannin bodies it is very suitable for topping with basic dyestuffs in order to modify the shade.

PERSIAN BERRIES.

This product is put on the market in the form of extract, which is obtained by extracting the unripe berries of rhamnus. It is not now used in dyeing, but still finds use in calico printing for producing yellows and allied shades with various mordants in steam styles.

COCHINEAL.

The colouring principle of this product is carminic acid, which is obtained from the female insect *Coccus cacti*, which is found in Guatemala and Mexico. It used to be applied in conjunction with tin and aluminium mordants for scarlet and crimson shades respectively, but since the introduction of the azo scarlet dyestuffs it has fallen into disuse. The scarlet coats of the British army were formerly dyed with cochineal, but the adoption of khaki gave cochineal its deathblow. It only survives in the scarlet of hunting coats. It may be dyed by the two bath or single-bath process. For the two-bath process equal parts of stannous and stannic chloride in conjunction with oxalic acid were used as the mordant: for the single-bath process stannous chloride and hydrochloric acid in conjunction with the cochineal were used.

The presence of iron and copper should be avoided, since they dull the shade.

MINERAL DYESTUFFS.

Mineral colours are produced by precipitating coloured metallic salts within the fibre. Their use is chiefly confined to the vegetable fibres and yield shades of extreme fastness to light and washing except Prussian blue, which is turned brown by alkali.

PRUSSIAN BLUE.

This colour possesses great beauty of shade coupled with extreme fastness to light, but it has fallen into disuse owing to the fact that it is turned brown by alkalies due to the formation of ferric hydrate. The methods of its production will therefore be only briefly mentioned.

Silk.—It is used in the dyeing of silk black with logwood to beautify the shade (see p. 187).

Wool.—The production of Prussian blue on wool depends upon the fact that acid solutions of ferro- and ferricyanides decompose to produce Prussian blue. Wool is dyed by entering into a cold bath containing 10 per cent. potassium ferricyanide and 20 per cent. sulphuric acid, raising the bath carefully to the boil in one hour and dyeing one hour at the boil. Nitric or hydrochloric acids may be substituted for the sulphuric acid, whilst the addition of 1–2 per cent. stannous chloride to the dyebath after it has boiled half an hour brightens and reddens the shade.

Cotton.—This fibre is dyed by a different method to wool in that the cotton is first dyed iron buff (*q.v.*), and then the blue is developed by working in a cold dyebath containing acidified potassium ferrocyanide. The depth of the blue developed is controlled by the amount of ferric oxide precipitated on the fibre when dyeing the iron buff.

CHROME YELLOW AND ORANGE.

These two colours are produced by double decomposition of lead acetate and sodium bichromate producing normal lead chromate (yellow) and basic lead chromate (orange). These colours are extremely fast to light and washing: they are, however, liable to be dusty and loose shades, which are dangerous in view of their poisonous nature. They are not much used now beyond a little for export to the East. They are only applied to vegetable fibres. The following is one method of working :—

Work the well-boiled cotton for fifteen minutes in a cold bath of lead acetate 10° Tw.: wring out and without rinsing pass through cold clear lime-water 1½° Tw.: wring out, pass without rinsing through a cold bath containing 2½ lbs. sodium bichromate per 10 gallons water made distinctly acid with hydrochloric acid. Wash off well, repeat again to get the depth, soap and dry. To obtain chrome orange, pass before soaping through a boiling bath of milk of lime –1° Tw.

IRON BUFF.

This colour is fast to light, boiling soap and alkalies, but is not fast to acids. It is, however, still used for fast buff shades. The colour consists of ferric hydroxide in various stages of hydration. It is produced by padding a ferrous salt solution on the cloth, then fixing with an alkali and oxidizing by air passage or by passing through a weak solution of bleaching powder. The shade obtained depends upon the strength of the ferrous salt bath and the number of impregnations given.

MANGANESE BRONZE.

This colour is produced in a similar manner to iron buff by which manganous hydroxide is precipitated on the fibre and then oxidized. Manganous chloride is the salt which is used for impregnation purposes.

METALLIC OXIDE KHAKI.

This colour possesses extraordinary fastness to all reagents: its only drawback is that cloth dyed with it is difficult to sew due to the deposition of so much metallic oxide within the fibre. It is applied to vegetable fibres only and usually in the form of piece. It is a difficult colour to apply successfully and requires great manipulative skill. It has been used for army cotton equipments, but the demand of the present war has also forced the dyeing of cotton khaki with sulphur dyestuffs to maintain the output, but the shade obtained thereby is nothing like as fast as the metallic oxide khaki.

The dyeing of metallic oxide khaki was patented (No. 11456) in Great Britain in 1884 by E. A. Gatty of the firm of Gatty & Co. in Preston, who have made a speciality of the commercial dyeing of this colour. The method patented was padding with chrome alum and ferrous sulphate, then precipitating the oxides with alkali. The shade was varied from olive through khaki to brown by altering the proportions of chrome and iron.

The shade obtained by the above process was not fast to acids. E.P. 7041, 1897, taken out by V. H. Gatty of Gatty & Co., Preston, protected a process for making the khaki fast to acids. The method patented was a passage through a boiling bath of sodium silicate 2° Tw.

The following is a typical recipe for khaki :—

Padding Liquor—

$33\frac{1}{3}$ parts chromic alum.
3 parts ferrous sulphate, 90° Tw.
5 parts pyrolignite of iron, 25° Tw.
59 parts water.

The bleached cloth is padded four times through the above cold liquor, then passed four times through a boiling soda ash bath containing 5 lbs. per 10 gallons, then washed well.

The above procedure is repeated three times without drying the cloth, which is then dried and steamed for one hour at 1 atmosphere pressure. Finally the cloth is passed through a boiling bath containing 5 lbs. sodium silicate 52° Tw. per gallon, washed, lightly soaped and dried.

The above details will enable one to realize why great manipulative skill is required to produce the same shade regularly when the material has to pass through so many operations.

For further details the reader is recommended—

" Khaki auf Baumwolle," by Dr. Theis.

SECTION XIV.—THE VALUATION AND DETECTION OF DYESTUFFS

THE valuation of dyestuffs is a much more difficult task than many people imagine, since by valuation is meant not merely money value tests of a dyestuff, but determination of its properties. Few people so exhaustively test a dyestuff as is necessarily carried out in a dyestuff manufacturer's experimental dyehouse. This is easily understood when it is remembered that a dyestuff manufacturer offers his dyestuff to all colour-consuming trades, whilst individual dyers confine their tests to the well-defined limits of their own trade.

In testing dyestuffs in the laboratory efforts should always be directed at imitating as far as is possible within the limits of the laboratory the actual conditions obtaining on the practical scale. The same volume of liquor should be used, the same length of time of boiling, the same length of time in dyeing, etc., can be easily carried out in the laboratory. It is when one attempts to imitate "potting," milling, etc., that difficulties arise. When comparative dye-tests are carried out the same conditions of temperature and vigour of boiling must be observed in all the dyepots. To this end a bath with suitably perforated lid holding 4–6 dyepots should be used. The bath should be charged with a solution which can be heated to a temperature of 120–130° C., which will ensure the water in the dyepots actually boiling. The author always uses calcium chloride as being both cheap and effective, whilst sodium nitrate is also used. Glycerine used to be employed, but it should be avoided owing to its objectionable smell on continual heating. Calcium chloride solution has one drawback in that in cold weather it sets in a solid lump which may crack the bath, whereas sodium nitrate falls in fine crystals. Steam heating should always be used in preference to gas, because the latter soon creates a foul atmosphere, if the baths are in constant use. If gas must be used the baths should be made of iron, and not copper, because the smell from gas-heated iron baths is nothing like so bad as gas-heated copper baths. If steam is used, have closed copper coils, which will withstand boiling calcium chloride for years. Steam heating is not only more healthy, but it is more economical. Steam at 60 lbs. pressure in a 2-inch copper coil will keep a bath containing 15 dyepots of 750 c.c. capacity boiling with only one-eighth of a turn of the valve. Many use plain water-baths, which makes it impossible for the water in the dyepots to boil. Tests carried out in such a bath are misleading in their results, especially with alizarine and chrome dyestuffs. The dye vessels used for small tests should be porcelain.

When testing a colour against a standard it is absolutely essential that a dyeing of the type should be made every time, because a slight variation of the conditions of boiling, etc., are sufficient to vitiate the tests from a comparative point of view. Comparative dyeings must always be made side by side in order to ensure that the dyeing conditions have been identical. This is a point which is frequently overlooked.

In carrying out tests of a colour account must always be taken of the average percentage which is used in practice. It is far more sensible to test a cotton sky blue at ¼ per cent. than at 2 per cent., because ¼ per cent. shade is the one more often dyed; on the other hand, fast chrome blacks should be tested at 6 per cent. rather than 1 per cent., because 6 per cent. is more frequently dyed in practice. Moreover, strength of shade is more easily judged in a weak shade than a strong shade, provided the colour is homogeneous—it is the author's custom to dye a 1–2 per cent. shade of a black for strength of colour and a full shade to determine the tone of the black.

The following are some of the usual tests through which a dyestuff is put:—

Light.—In carrying out tests for fastness to light regard must be had for the use to which the fabric on which the colour is to be used is to be put. For instance, it is no use making a severe exposure of a direct cotton dyestuff which is going to be used for cotton linings, which will never be exposed to light. On the other hand, a colour which is going into tweeds should have at least one month's exposure in the open in summer weather, without any protection. The author always exposes all mordant, acid, vat, and sulphur dyestuffs on a roof in the country facing south, without any protection whatever from rain, etc., but basic and direct cotton dyestuffs (unless known to be very fast) are always exposed under glass. The objection raised against outside exposure without protection is that the patterns get dirty. This is not disputed, but so do clothes get dirty in actual wear, moreover, the majority of colours exposed in the open are sufficiently fast to withstand the light soaping necessary to remove the dirt. If it is known that the particular colour will not withstand washing, then recourse may be had to a benzine soap and benzine.

As regards length of exposure, one month's unprotected exposure in the summer months is ample to show whether it is as fast as the standard chosen for comparison. There are very few colours except guaranteed fadeless colours which need be exposed any longer, because this length of time will have a considerable effect on the average colour. The author has made it a practice of exposing patterns of suits he has worn. He has always found without exception that a colour which withstood one month's exposure was sufficiently fast for the lifetime of the suit.

If the cloth is for sailors' uniforms or for continuous and unusual exposure, then special precautions must be taken. Such cloths are frequently nailed to the mast during an out-and-home journey to Australia, or similar extreme measures taken.

It is my experience that many people hold a very exaggerated opinion of the fastness to light of many colours. Quinoline yellow has a reputation for fastness to light, but a comparative exposure against xylene fast yellow soon shows how relatively fugitive it is. Again, sulphoncyanine s a colour which has a great reputation for fastness to ight, but a month's exposure at the seaside will practically leach it, though it is widely used without complaint in the lyeing trade. If it is exposed against indocyanine B or lizarine blue its comparative lack of fastness is soon pparent.

Milling.—This process is most satisfactorily tested by aving the pattern stitched on to the end of a piece which s going through the particular milling process in question, ecause this process varies largely according to the class f cloth and the particular finish required.

The author's method consists of dyeing the colour on ome yarn and knitting it in a hand-knitting machine along with white wool, cotton, and silk, if necessary. This fabric s run through the rollers of a domestic wringing machine, which are driven from a shafting. Underneath the rollers is fitted a trough with an open steampipe in which soap and soda solution is put and heated to 100° F. (40° C.). Guiding bars are fitted in the trough so as to ensure that the fabric constantly passes through the soap liquor. My twelve years' experience of this machine has shown that a colour which withstands the above test has never failed to stand in practical working. In this machine a colour as fast to milling as sulphur black may be milled down to a grey in half an hour. A milled pattern must be examined for loss of depth, change of shade, and bleeding into adjacent white.

Failing the above the pattern should be vigorously rubbed between the hands with strong soap and soda solution, then allowed to lie in the solution half an hour.

Washing.—The following method is very satisfactory. Make up a solution of 5 grs. soap and 3 grs. soda ash per 1000 c.c. of water. Use this solution at 100° F. (40° C.) for washing; rub the material, along with white wool, cotton, and silk, between the hands for 15 minutes, allow to lie in the soapsuds for 15 minutes, wash off, first in warm water to remove the soap, then in cold water, finally dry. Alkali is omitted if the test has not to be severe. Loss of depth, change of shade, and staining of white should be carefully noted as against standard.

It is a very common practice in making milling and washing tests to plait the dyed yarn with white wool and cotton. The author has strong objections to this procedure for the following reasons. It is extremely difficult to wash out of the centre of the plait the last traces of soap and soda, so that when the plait is dried the traces of soap and soda—as drying proceeds—become more and more concentrated, and the test amounts to heating the plait with strong soap and soda. If knitted fabric is used the soap and soda may be easily washed out of the same, moreover it is much the more convenient way for mounting the tests in reference books.

Potting.—This is difficult to imitate in the small way, but the following method gives good comparative results, if a standard is always tested at the same time. Put a piece of the cloth to be tested between white flannel and cotton, wet them out thoroughly, then wrap them tightly round a glass rod and tie tightly round with string. Immerse the rod in water at the temperature at which the particular potting is carried out for the number of hours taken on the big scale. Note if the water is stained, also change of shade and staining of the white wool and cotton ; silk is also taken if necessary.

Stoving.—This is a test which is best carried out under the actual conditions under which the colour will be stoved in practice. Failing this the following method gives good results. Stitch the colour between white wool and cotton, wet out thoroughly, then hang on a wooden stand, over which place a bell-jar, put an iron box of sulphur under the bell-jar and ignite by dropping a red-hot iron bolt in it. Allow air into the jar until the smell of sulphur dioxide is pronounced outside the jar, put the jar down and put putty all round the bottom to keep the jar gas-tight. Leave like this for twelve hours, wash off, dry, then examine the pattern for change of shade and bleeding into the adjacent white.

Copper and Iron Vessels.—The use of copper and iron is increasingly common in dyeing owing to the steady adoption of dyeing machinery. Now, all dyestuffs may not be dyed in copper or iron vessels without definite change of shade, so that it is requisite to test new dyestuffs from this point of view. This may easily be done by placing a coil of copper wire or iron plate in the bottom of the dyepot whilst dyeing under exactly the same conditions another pattern without the metal in the dyepot. Compare results.

Hot Iron.—Many colours change their shade temporarily under heat, particularly direct cotton dyestuffs. This test is simply carried out by placing a piece of wet cotton cloth over half the pattern and ironing it dry with a hot iron. Compare the ironed portion with the other portion immediately after ironing and when the pattern has cooled down.

Carbonizing.—Soak the dyed wool half an hour along with the cotton in cold sulphuric acid, 7° Tw., then squeeze out. Now place in a porcelain dish and heat for one hour at 175° F. (80° C.), when the cotton should be completely carbonized. Wash off, neutralize with soda ash, wash off and dry. Compare the shade with some of the original pattern.

Acids.—Spot with 10 per cent. D.O.V. solution for mineral acids and acetic acid (30 per cent.) for organic acids.

Decatizing.—This is a test which is difficult to imitate on the laboratory scale, and is best carried out on the big scale when possible. Failing this fit up a small perforated cylinder with the steam supply; wrap this round with calico, blow the steam through till it is dry, then wrap on the pattern to be tested and blow the steam through the desired length of time.

Perspiration.—Dissolve 100 grs. salt and 100 c.c. acetic acid (30 per cent.) in 1000 c.c. water; thoroughly wet out the pattern to be tested and a piece of white wool and cotton, roll together with the pattern between the wool and cotton, then incubate in a test-tube for 24 hours at 100° F. (40° C.). Examine for staining and loss of shade. A more direct test is to get a stoker to wear a pattern.

Alkali.—Dissolve 100 grs. salt and 10 grs. soda ash in 1000 c.c. water; treat exactly in the same way as for perspiration above. Examine for loss of shade and staining. Another method is to spot milk of lime (20 per cent.) on the pattern, allow to dry, then brush off.

In making trials of the various classes of dyestuffs the following points should be particularly noted:—

Acid Dyestuffs.—For wool trials use thirty times liquor on the weight of the wool; for silk trials use fifty times liquor. In the first dye trial, start cold, raise up to boil in half an hour, and dye boiling half an hour. Notice the rate of dyeing. If the colour dyes on quickly it will, as a rule, dye unlevel, whereas if it dyes on slowly and still dyes on slowly at the boil, it will be a level dyeing colour. If it dyes on quickly, reduce the acidity of the dyebath and so work out the best conditions for dyeing that particular colour.

Levelling is best tested as follows. Prepare a boiling dyebath with a small percentage of the colour and 5 per cent. sulphuric acid only—no Glauber's salt; throw in a piece of dry, tightly woven cashmere cloth, and work quarter an hour at the boil. Compare the result with a standard colour of admitted excellent levelling properties like patent blue carried out under identical conditions at the same time.

Penetrating powers are tested under the same conditions, using a piece of closely milled woollen hat felt boiling half an hour; cut the felt in half and compare the degree of penetration.

To judge if a colour is suitable for salting, *i.e.* adding to the boiling dyebath, proceed as follows. Assume, for example, a red is being examined. Dye a piece of cloth or yarn with 0·1 per cent. quinoline yellow, 0·1 per cent. patent blue A, 3 per cent. sulphuric acid—Glauber's salt is designedly omitted; after boiling half an hour add 0·1 per cent. of the red, being tested, and boil a further half-hour. After washing off and drying examine the material for evenness of shade and penetration. If satisfactory from both points of view it may safely be used for salting purposes. In all cases an accepted standard of red must be dyed at the same time under identical conditions.

Mordant Dyestuffs should be tested by all three methods detailed in Section IV., taking particular care to test on all forms of chrome mordant given therein. The properties to note are solubility, rubbing, levelling, milling, light, and sensitiveness to metals.

Direct Cotton Dyestuffs should be dyed with twenty times liquor cold, 100° F. (40° C.), 140° F. (60° C.), 175° F. (80° C.), 195° F. (90° C.), and boil, and the affinity noticed at the different temperatures, because if it has a good affinity at low temperatures it will be useful for mixed materials, burl dyeing, and artificial silk. Exhaust tests should also be made in order to ascertain if the colour exhausts well or not, and thus determine if it will be necessary to work it in a standing bath. Assuming the colour is a black exhaust tests are carried out as follows. Prepare a dyebath with 6 per cent. black, ½ per cent. soda ash, 30 per cent. salt. Enter the cotton warm, raise to boil, and boil half an hour, wring out the cotton well, returning the liquor to the dyebath, then make up the volume of the dyebath to the original volume, add 10 per cent. salt, but no colour, and dye in it for half an hour at the boil an equal weight of cotton to that originally taken. This second test is what is called the exhaust test, and shows how much colour is left in the dyebath. Direct cotton dyestuffs vary very much in the amount of colour they leave in the dyebath.

The special points to which attention should be paid are light, washing, acids, hot-pressing; levelling should be tested on similar lines to those given under acid dyestuffs.

Sulphur Dyestuffs.—The first thing to determine is the proper amount of sodium sulphide required to give the best results. Dye trials should be carried out with varying amounts of sodium sulphide. Exhaust tests should be carried out as detailed under direct cotton dyestuffs.

The dyeing of sulphur dyestuffs on the small scale is exceedingly difficult, and the results so obtained are never as good as those obtained on the large scale. In making comparative dyeings great care must be taken to see that all the dyeings are treated exactly alike, so as to ensure that they oxidize alike. To this end the patterns should be plunged straight from the dyebath under cold water, washed off together, squeezed together, and dried together. It is no use comparing dyeings of one hank which has been dried straightaway with another hank which has been allowed to hang on a peg in the wet state for 15 minutes before drying. Owing to the fact that all dyeings of sulphur dyestuffs oxidize up on keeping it is advisable to chrome off all dyeings which are made to match dyed patterns, otherwise the newly made dyeing will not be comparable with one which has been dyed some time.

The properties which should be specially noted are light, milling and fastness to boiling acids.

Basic Dyestuffs.—The chief points to determine are solubility and the proper amount of tannin required as the mordant to give the brightest and fastest shades.

THE IDENTIFICATION OF DYESTUFFS.

The identification of dyestuffs has of recent years been elaborated by Green and collaborators which have now been collected together and published in book form under the title of "Analysis of Dyestuffs" (Griffin). The reader who wishes to go into this subject in detail is referred to this volume. All these tables refer to individual dyestuffs, whereas a large majority of the shades which come into the hands of a dyer are compound shades of three colours. Moreover, in everyday work such elaborate tests are not required because in the majority of cases the dyer only requires to know what class of dyestuffs have been used to dye the pattern concerned. In commercial dyeing the price being paid for the dyeing usually enables a dyer to form an accurate opinion as to what dyestuffs may be used, whilst the class of material to be dyed is also a governing factor.

The following lists of tests make no claim to completeness, but are simply those which are used by the author in everyday routine work :—

Basic Dyestuffs.—Boil a pattern with alcohol or methylated spirits, when the colour will be dissolved off the fibre. Evaporate off the alcohol, redissolve the colour in water in which tannin-mordanted cotton may be redyed the original colour.

Direct Cotton Dyestuffs.—Boil some of the pattern with ammonia and water, when the colour will be largely stripped. Lift out the pattern, evaporate off most of the ammonia and add a little soap and water. Boil a piece of white cotton in this solution, when it will be dyed the colour of the original pattern. A developed dyestuff may bleed a little, but it will not dye the white cotton to the same extent.

There is no positive test to distinguish a developed dyestuff from a direct cotton dyestuff, and now this position has been further complicated by the formaldehyde after-treatment of certain direct cotton dyestuffs which improves their fastness and makes them intermediate between direct and developed cotton dyestuffs. The following method used by the author enables with practice a fairly accurate judgment to be formed. Wet the pattern to be examined, and place it between wet bleached mercerized sateen and iron it dry with a hot iron. Notice the amount of bleeding on the sateen. Direct cotton dyestuffs bleed distinctly, a well-dyed developed dyestuff will practically not bleed, a direct cotton dyestuff after-treated with formaldehyde will bleed to a degree between the two. This is not given as a positive test, but a skilled observer can usually form an accurate judgment.

Developed and Direct Cotton Dyestuffs.—These are permanently decolorized by boiling with tin crystals and spirits of salts, hydrosulphite, or titanous chloride. Basic dyestuffs and vat dyestuffs may be temporarily decolorized, but they regain their colour on washing. Logwood black, catechu brown, aniline black, and sulphur dyestuffs are not completely decolorized. A developed primuline shade is reduced to the original yellow primuline bottom.

Sulphur Dyestuffs.—Boil in a test-tube with tin crystals and spirits of salts. Sulphuretted hydrogen will be evolved, which may be detected by placing a piece of filter paper, moistened with lead acetate solution, at the mouth of the test-tube. The paper will be turned from brown to black. A slight yellow coloration on the paper must not be taken as indicating a sulphur dyestuff; the coloration should be definite with a metallic lustre. When there is any doubt, do a blank test to test the purity of the chemicals.

Logwood Black.—Boil with a little dilute acid, when the familiar red coloration will be given.

Aniline Black.—Place a piece of the pattern in D.O.V., allow the fibre to char, now dilute with water; a pale green solution is a certain indication that it is aniline black. A sulphur black topped with aniline does not give this reaction.

Distinction between Aniline Black, Sulphur Black, and Sulphur Black topped with Aniline.—Place patterns in bleaching powder solution (about 4° Tw.), which is just under the boil. The sulphur black is completely bleached, whereas an aniline black goes nut-brown, and a sulphur black topped with aniline varies from a pale yellow to a brown, according to the amount of aniline which has been used in the topping bath. If one treats at the same time a pattern of a sulphur black, topped with a known amount of aniline, a rough estimate of the amount of aniline used may be formed with a little experience.

Turkey Red cannot be reduced with tin crystals and spirits of salts. Boil with a little titanous chloride, when the red immediately changes to a maroon; this is very characteristic, because other possible reds (on cotton) are decolorized.

Insoluble Azo Dyestuffs (Para Red, etc.).—Wrap a pattern between white calico and iron with a hot iron; the colour volatilizes on to the calico.

Indigo.—Spot the material with concentrated nitric acid, when pure indigo gives a bright yellow spot with characteristic green rim. Many other colours will give a bright yellow spot but do not give the green rim characteristic of indigo. This test in the hands of an experienced operator is very good, but an inexperienced one may easily be deceived by shades which are faked up to give the indigo spot. The two following points help to enable the detection of faked shades, viz.:—

1. If the spotted fabric is allowed to stand 24 hours the indigo spot does not deteriorate in colour, but the spot of a faked fabric usually does.

2. Pure indigo will give its characteristic spot with nitric acid of a lower concentration than the faked colour usually will. If one is suspicious of a fabric, then use nitric acid of as low a concentration as will still give the characteristic indigo spot on a fabric known to be dyed with pure indigo.

Indigo may be sublimed off the fibre by gently heating it in a test-tube, and the indigo will condense on the higher and cooler parts of the test-tube.

A very simple, yet effective, test for indigo on wool is to boil the wool with weak caustic soda until the wool is disintegrated; now add a little hydrosulphite after cooling down, and if indigo is present the indigo will be reduced and form the characteristic yellow solution with bronzy scum, in fact an indigo vat on a small scale.

Another simple test is to boil the pattern with strong sulphuric acid till the fibre is disintegrated, then dilute with water, when you will get a bright-blue solution of indigo extract. If the solution is masked by any bottoming or topping of the indigo, then dye a piece of wool in the solution, when it will be dyed the bright-blue shade characteristic of indigo extract.

Catechu Brown.—Not affected by acids or alkalis, nor decolorized with tin crystals and spirits of salts.

Acid and Direct Cotton Dyestuffs on Wool.—Boil with ammonia, when the average colour will be stripped more or less completely. Evaporate the solution down, add a pinch of salt, and see if it dyes cotton. If it does not, it is an acid dyestuff; if it does, it is a direct cotton dyestuff. Acid dyestuffs will be found to strip more easily than direct cotton dyestuffs.

Mordant Dyestuffs.—These are distinguished by their fastness to boiling ammonia. Fuse some of the pattern with soda ash and sodium nitrate in a platinum crucible; dissolve out the mass, make acid with acetic acid and take care to boil the solution to drive off all carbon dioxide, add a solution of lead acetate, when a yellow precipitate of lead chromate proves the presence of chromium. Iron and copper may also be looked for.

Potting Blacks.—It is sometimes desirable to distinguish between chrome blacks of the fast to potting and not fast to potting series. The following is a rapid means of doing so. Dilute concentrated nitric acid thirty times with water, boil the patterns two minutes in this, then wash off immediately. Non-potting blacks are practically destroyed by this treatment, whereas fast to potting blacks are not destroyed by this treatment, owing to their superior fastness to oxidation.

Vat Colours.—Drop the pattern into warm alkaline hydrosulphite solution, when the characteristic colour of the leuco compound will be formed, which in most instances, except indanthrene blues, are quite distinct from the dye in its normal state. The original colour returns on washing off the pattern and exposing to the atmosphere.